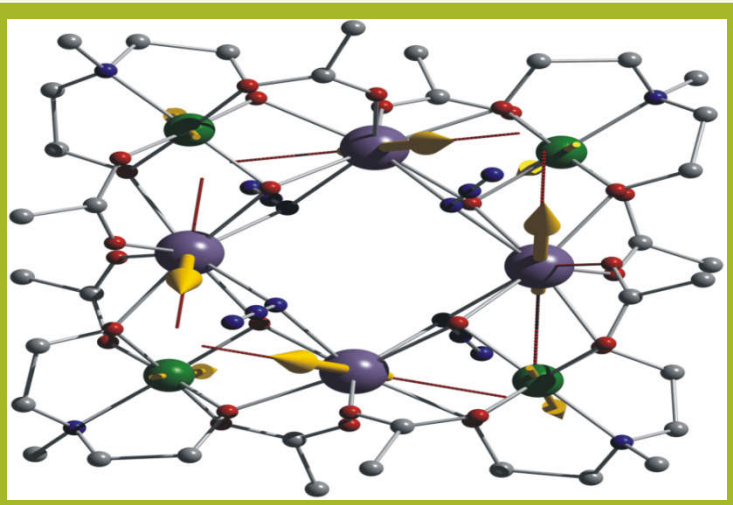


دانشگاه مازندران

University of Mazandaran

Theoretical Chemistry of Nanostructures

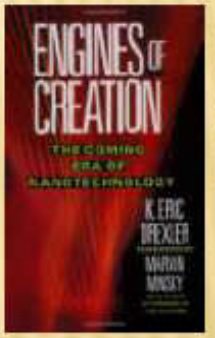
History of nanotechnology:

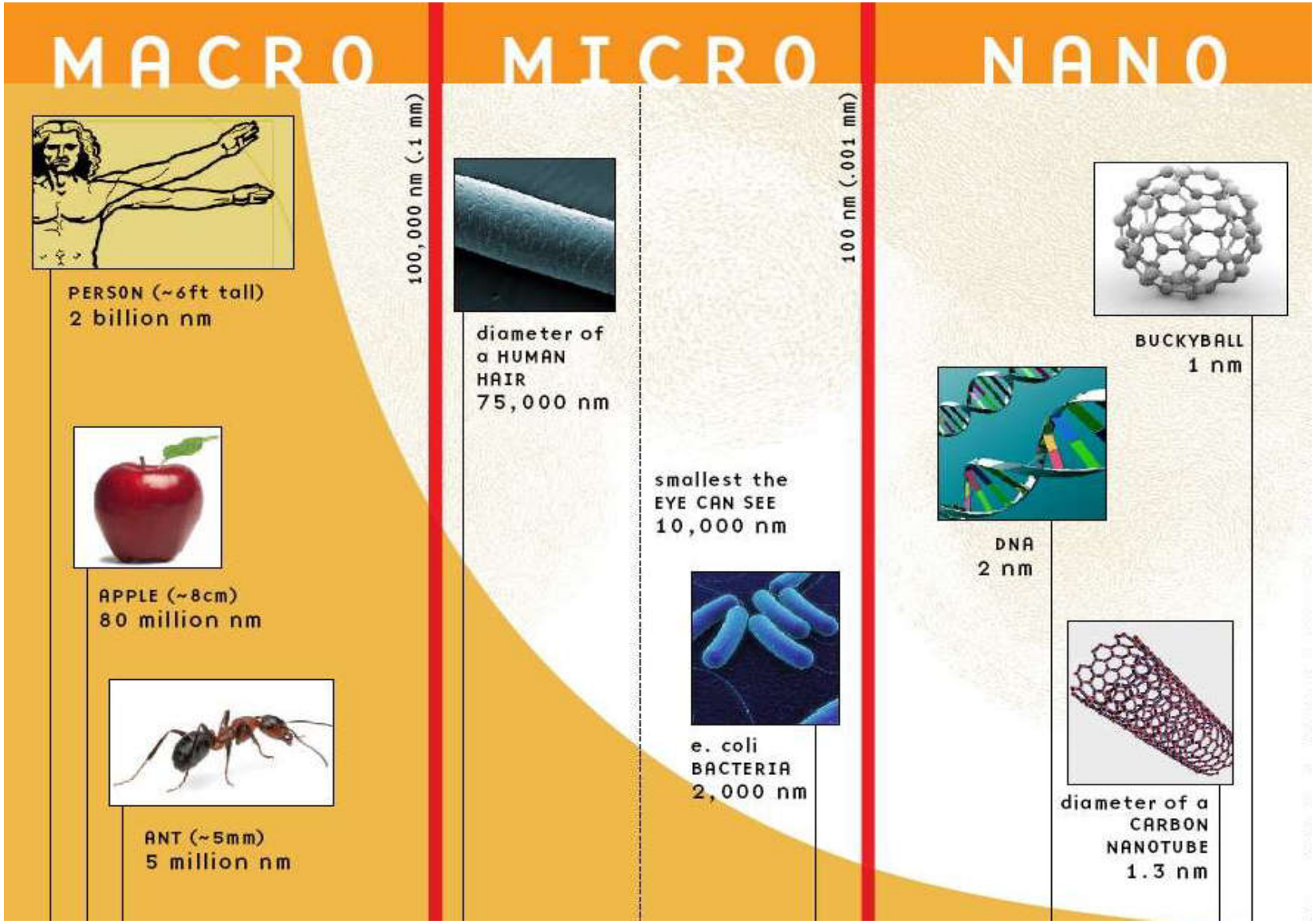
- It's rather difficult to describe the history of nanotechnology, is due to two principal reasons: 1) ambiguity of the term "nanotechnology" and 2) uncertainty of the time span corresponding to the early stages of nanotechnology development.

- Nanotechnology covers various types of physical, chemical and biological processes realized on nano level. Besides, nanotechnologies at the current stage of development are being constantly updated and improved, which explains why many concepts about principles of their implementation are not completely clear.

Nanotechnology is science, engineering, and technology conducted at the nano scale, which is about 1 to 100 nanometers.

- **~ 2000 Years Ago** – Sulfide nano crystals used by Greeks and Romans to dye hair
- **~ 1000 Years Ago (Middle Ages)** – Gold nano particles of different sizes used to produce different colors in stained glass windows
- **1959** – "There's plenty of room at the bottom" by **R. FEYNMAN->**
- **1974** – "Nanotechnology" - Taniguchi uses the term nanotechnology for the first time
- **1981** – IBM develops Scanning Tunneling Microscope
- **1985** – "Buckyball" - Scientists at Rice University and University of Sussex discover C_{60}
- **1986** – "Engines of Creation" - First book on nanotechnology by K. Eric Drexler. Atomic Force Microscope invented by Binnig, Quate and Gerbe
- **1989** – IBM logo made with individual atoms
- **1991** – Carbon nanotube discovered by S. Iijima
- **1999** – "Nanomedicine" – 1st nanomedicine book by R. Freitas
- **2000** – "National Nanotechnology Initiative" launched

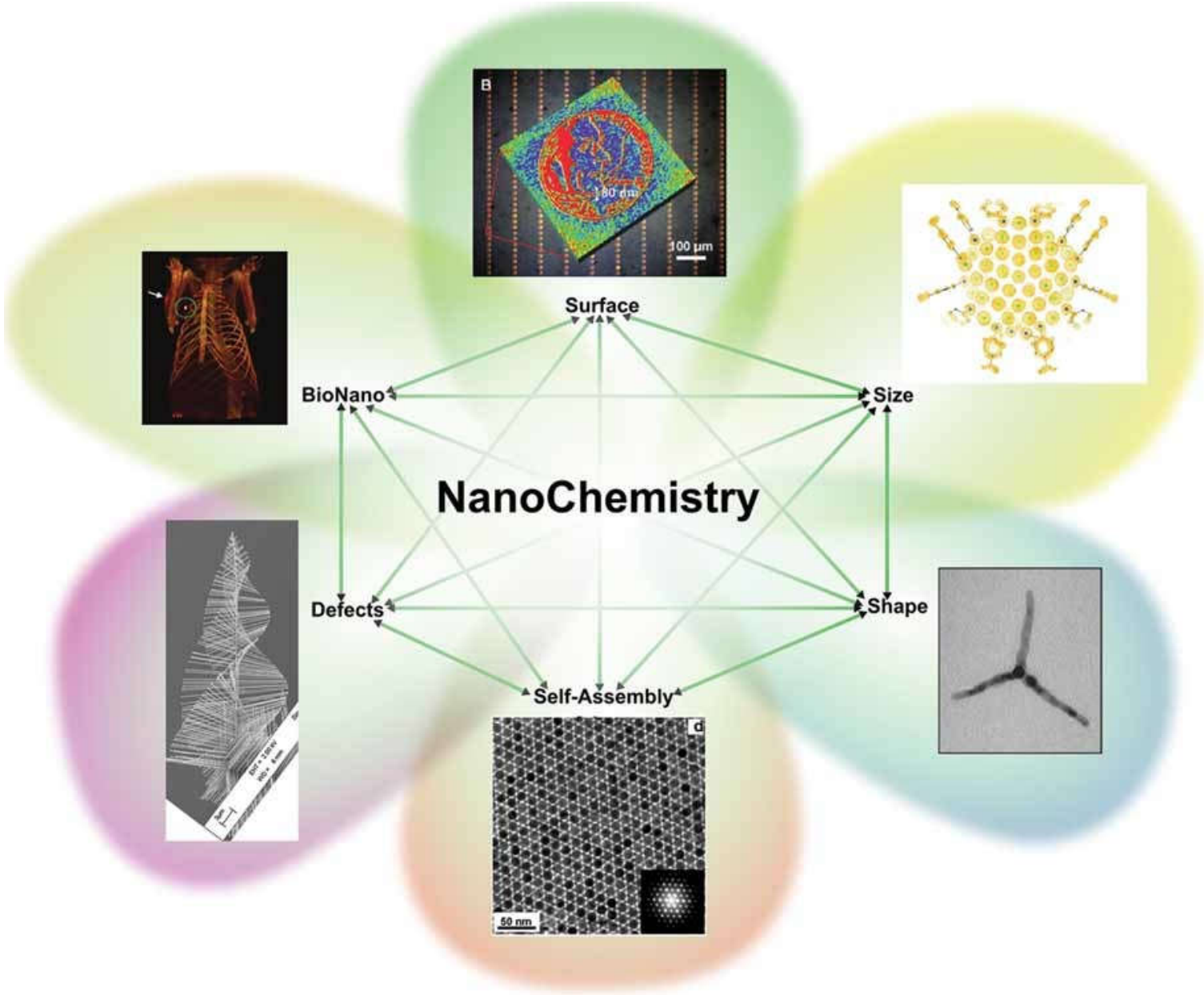


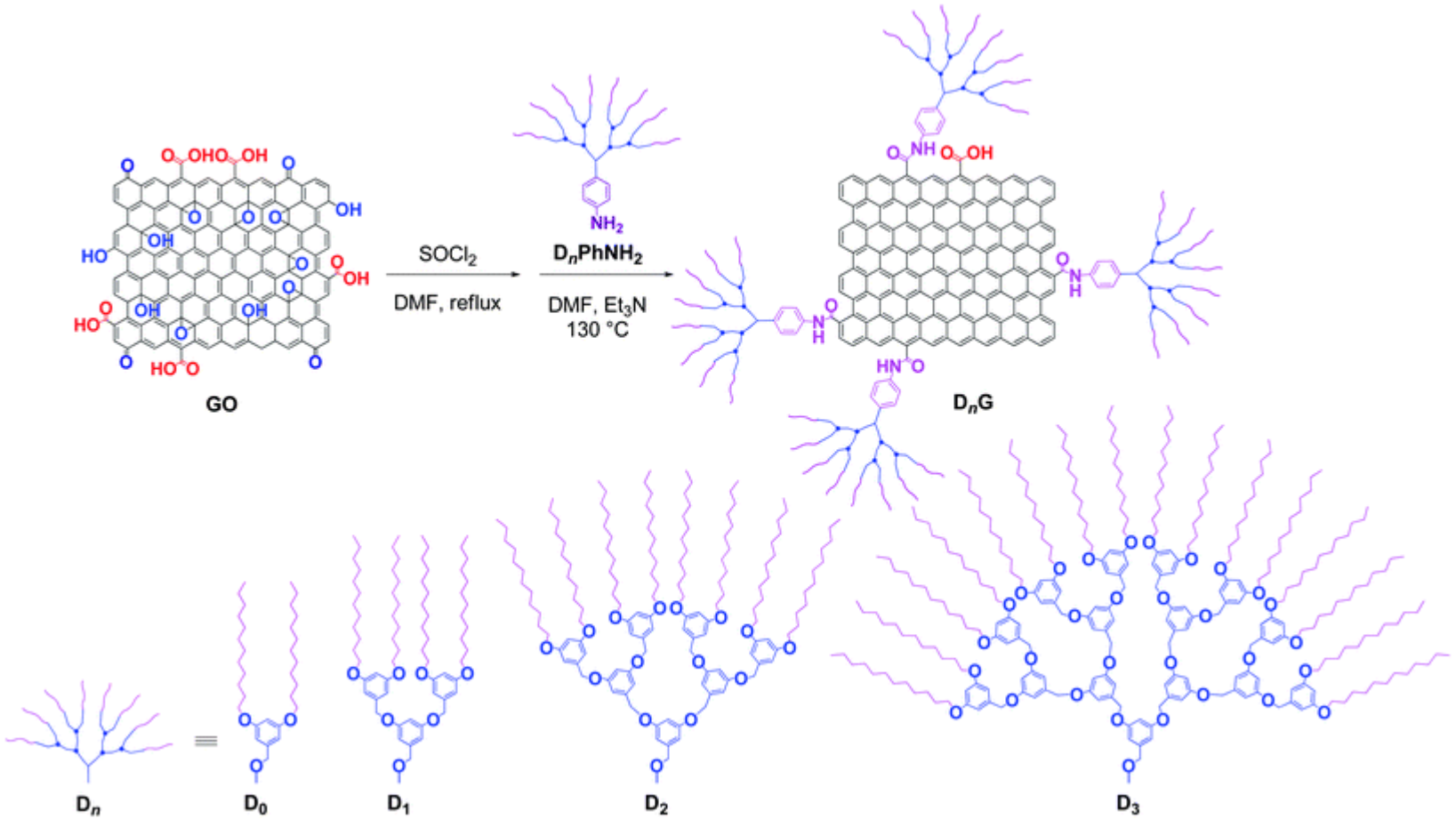

MACRO
MICRO
NANO
100,000 nm (.1 mm)
100 nm (.001 mm)
PERSON (~6ft tall)
2 billion nm
APPLE (~8cm)
80 million nm
ANT (~5mm)
5 million nm
diameter of a HUMAN HAIR
75,000 nm
smallest the EYE CAN SEE
10,000 nm
e. coli BACTERIA
2,000 nm
BUCKYBALL
1 nm
DNA
2 nm
diameter of a CARBON NANOTUBE
1.3 nm

Nanomaterials can be understood as the materials, which are characterized at least in one of three dimensions by nanometer scale concerning both the sample of a material as a whole and its structural elements.

Nanochemistry:

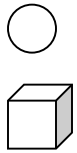
Utilization of synthetic chemistry to make nanoscale building blocks of different: Size and shape, Composition, Surface structure, Charge, Functionality. Also it deals with the reactions of nanoparticles and their compounds.


B
100 µm
Surface
BioNano
Size
NanoChemistry
Defects
Shape
Self-Assembly
d
50 nm

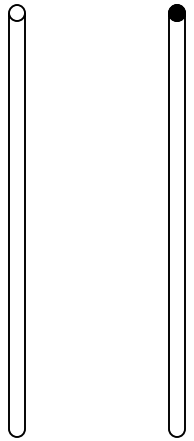

SOCl2
DMF, reflux
DnPhNH2
DMF, Et3N
130 °C
GO
DnG
Dn
D0
D1
D2
D3

Morphology or dimensions:

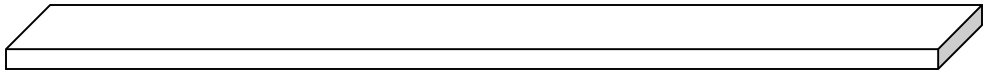
0-Dimensional

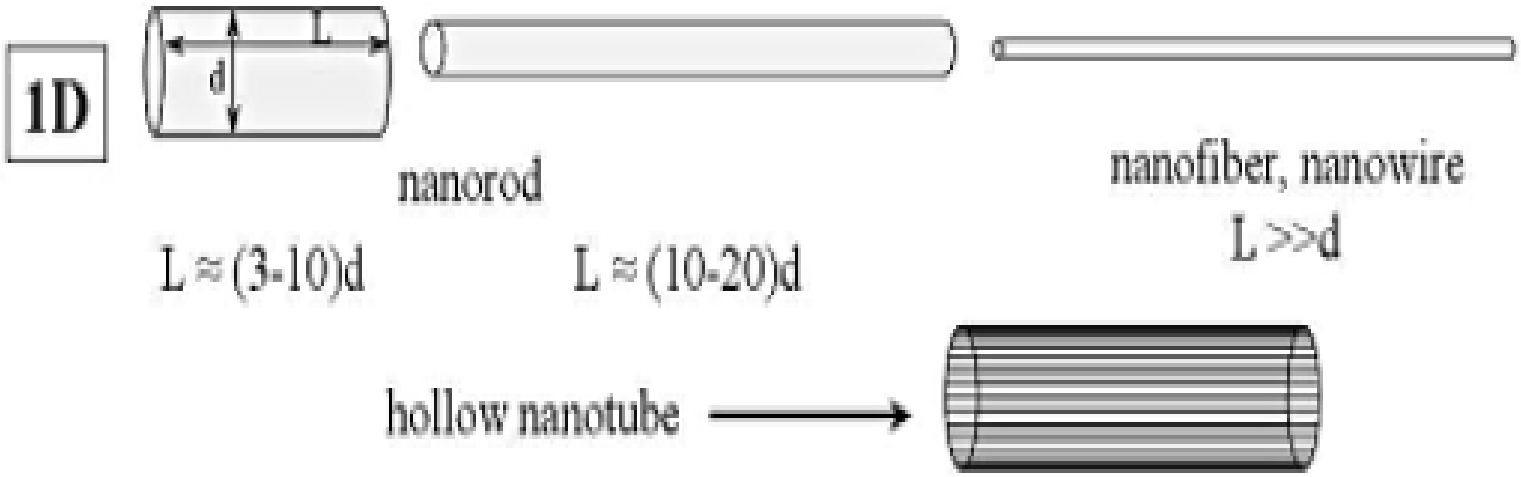


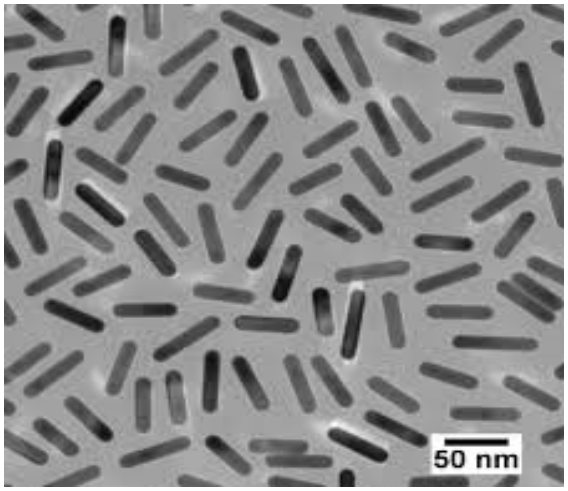
1-Dimensional

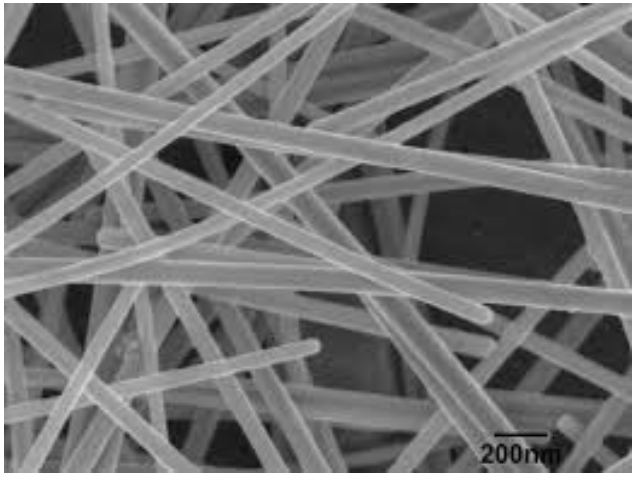


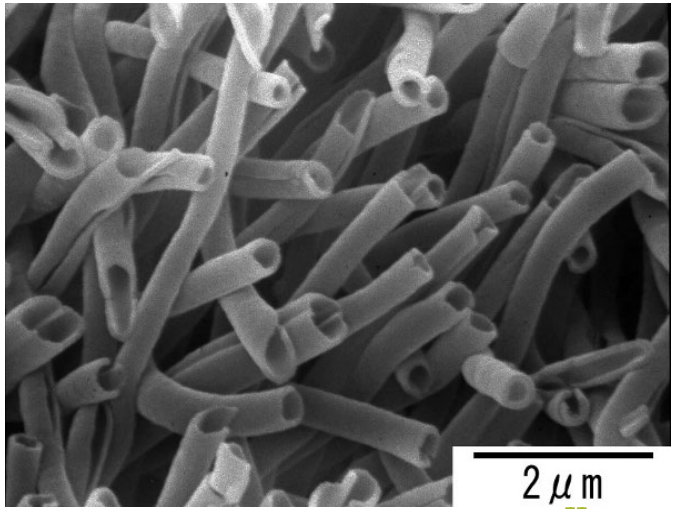
2-Dimensional

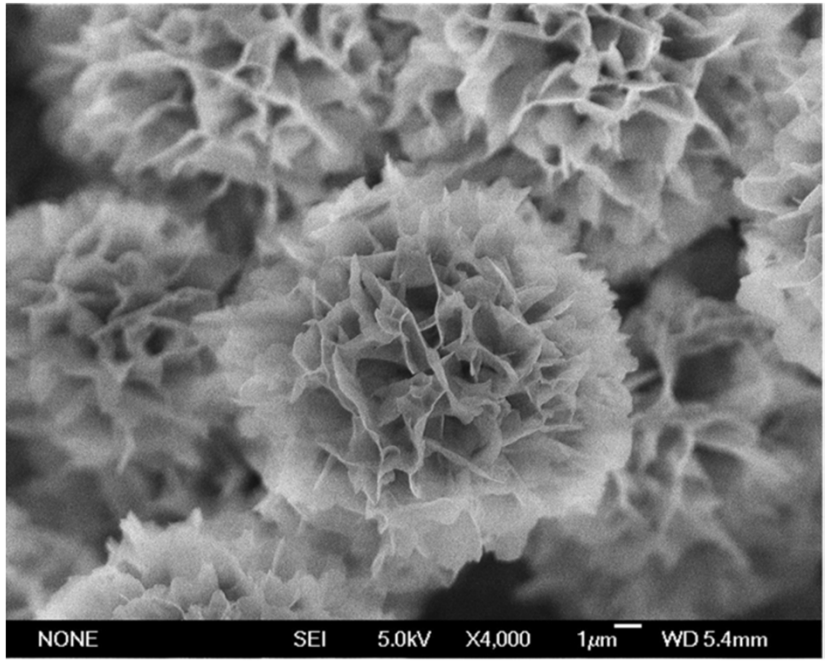


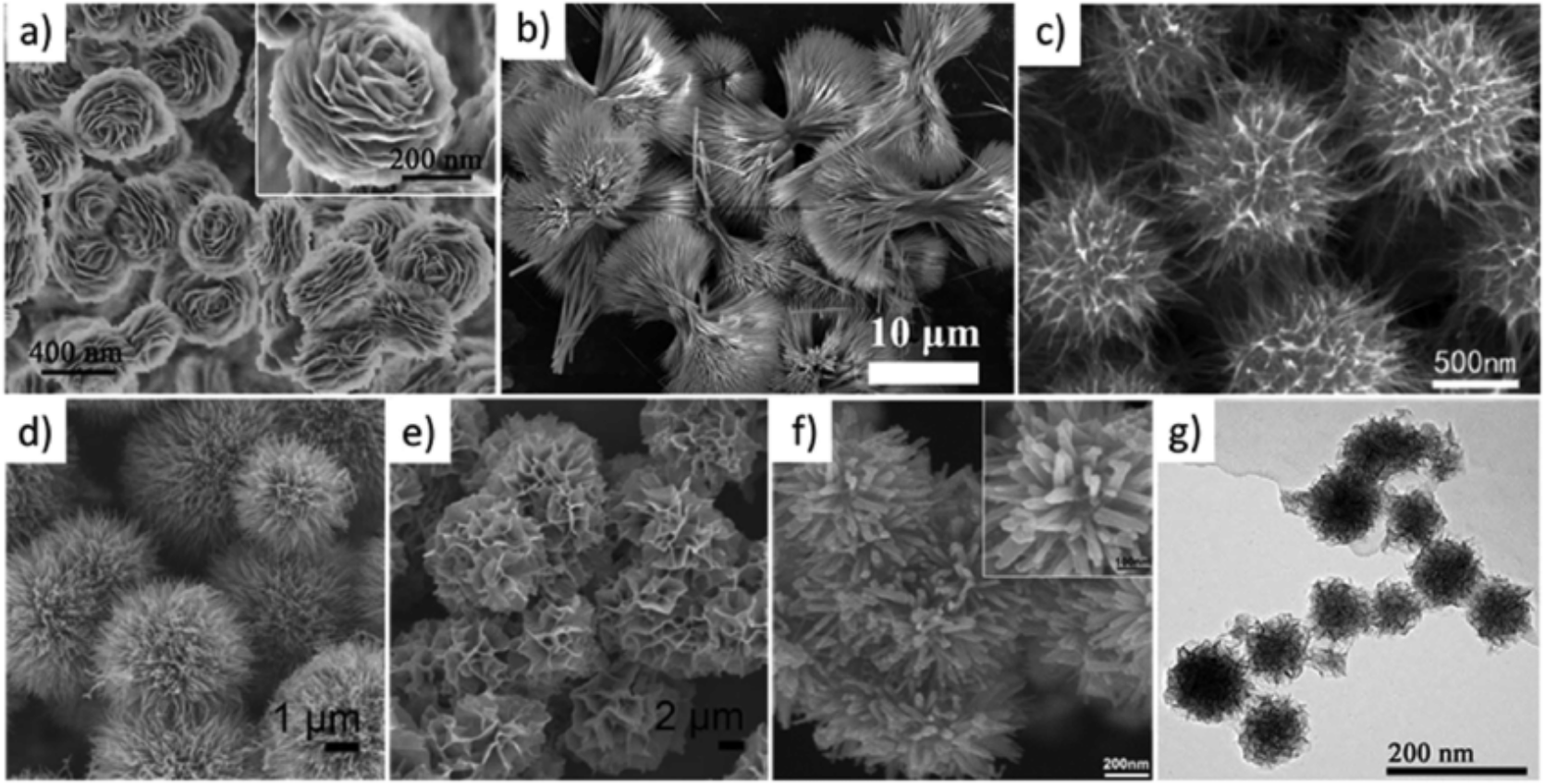

1D
L
d
nanorod
nanofiber, nanowire
L >>d
L ≈ (3-10)d
L ≈ (10-20)d
hollow nanotube


50 nm

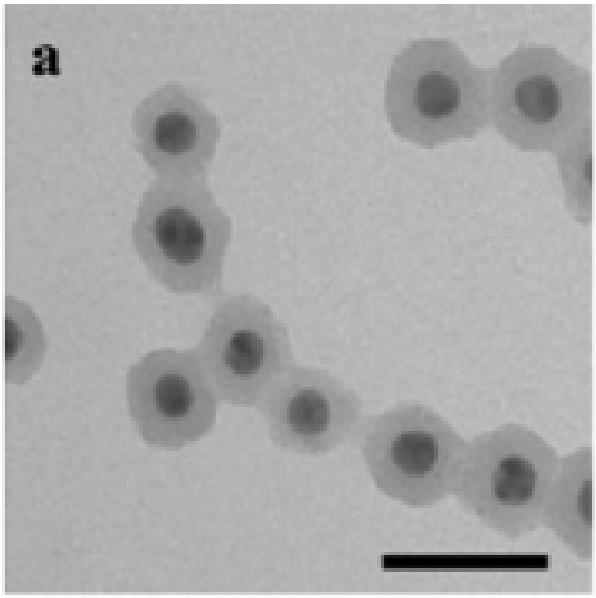

200nm

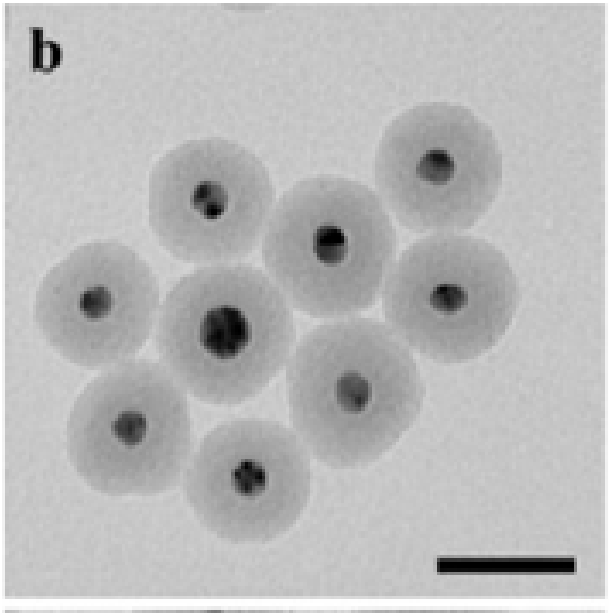

2 μm

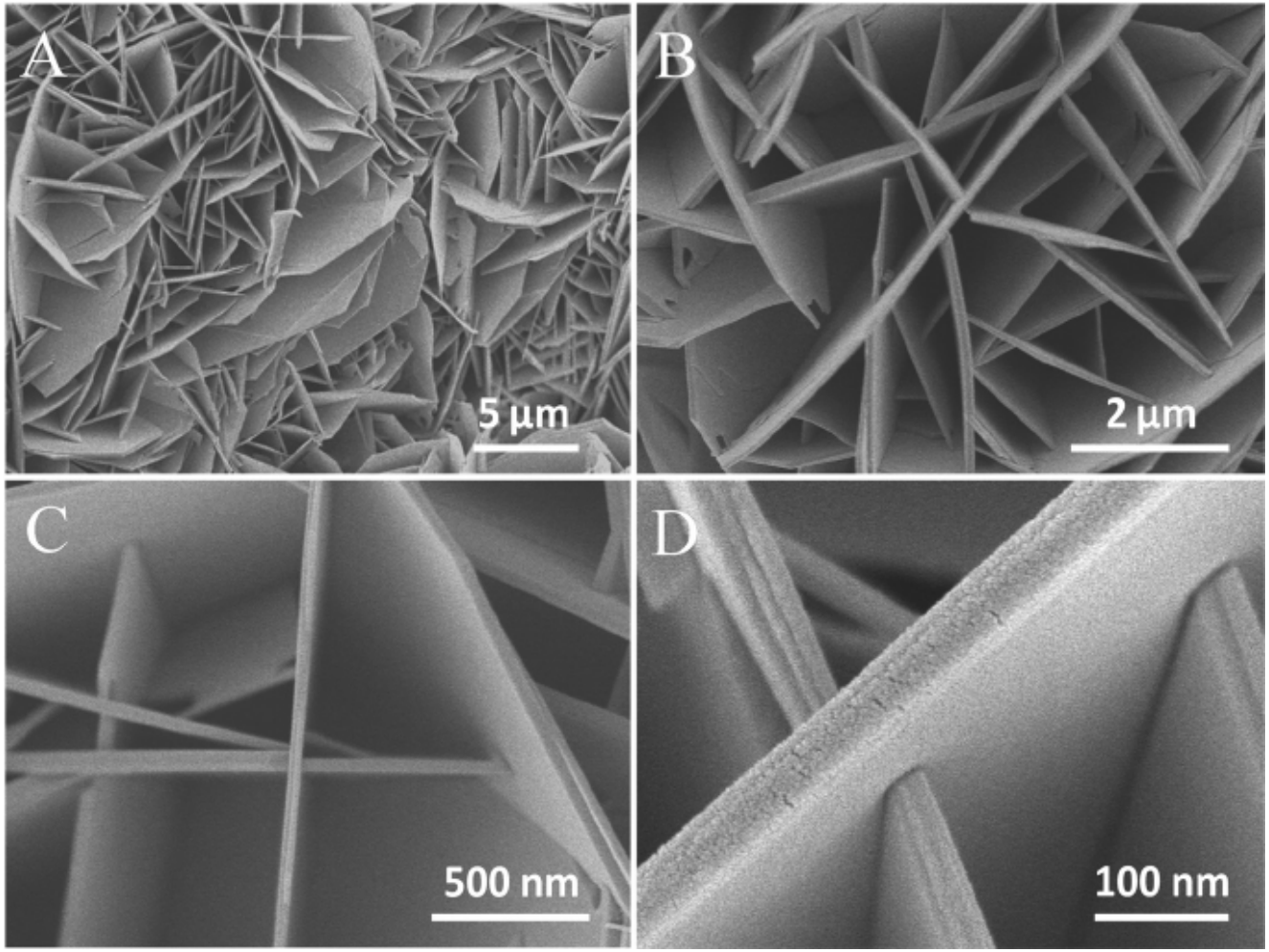

NONE
SEI
5.0kV
X4,000
1μm
WD 5.4mm



Hierarchical nanostructures


a

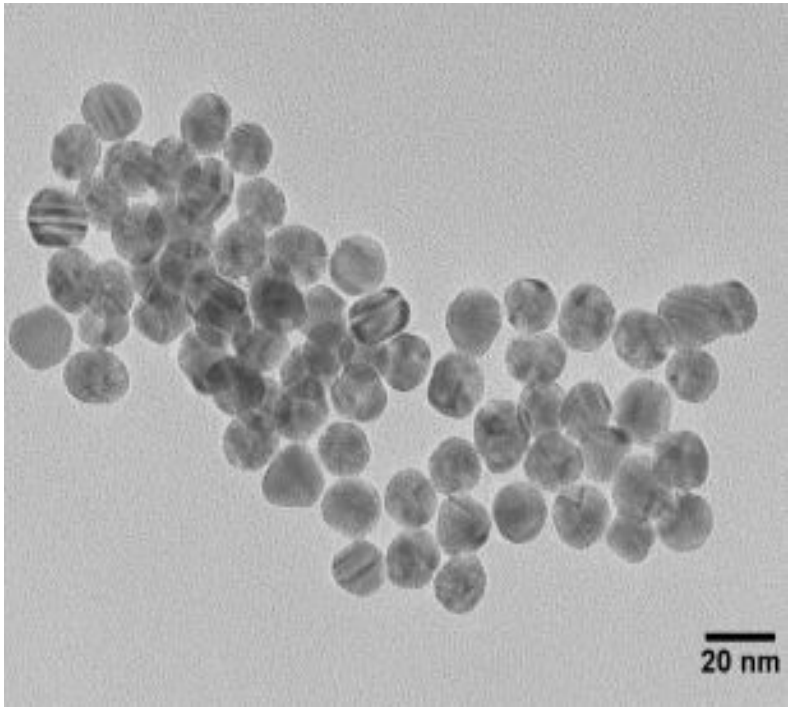

b

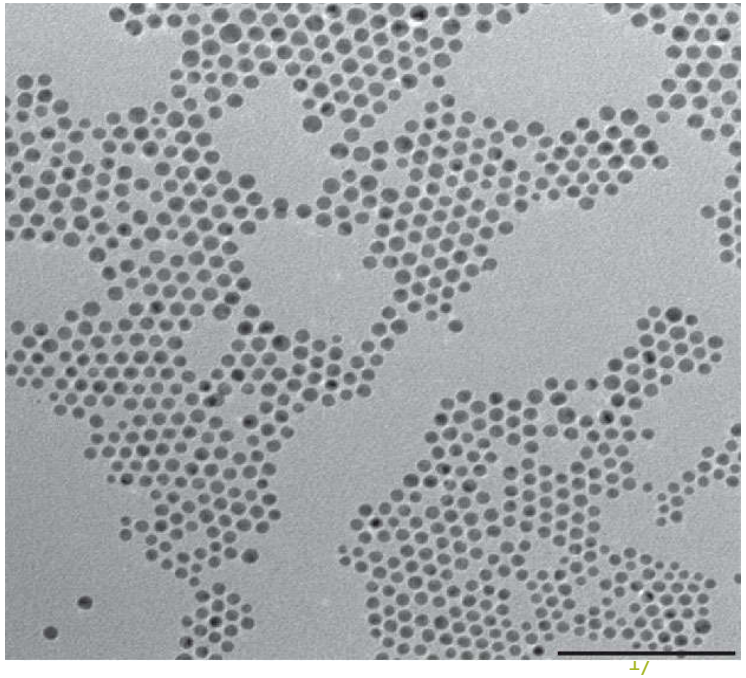

A
5 µm
B
2 µm
C
500 nm
D
100 nm

Nanoparticles:

Nanoparticles are the simplest form of structures with sizes in the nm range. In principle any collection of atoms bonded together with a structural radius of < 100 nm can be considered a nanoparticle.

These can include, e.g., fullerens, metal clusters (agglomerates of metal atoms), large molecules, such as proteins, and even hydrogen-bonded assemblies of water molecules, which exist in water at ambient temperatures.


20 nm

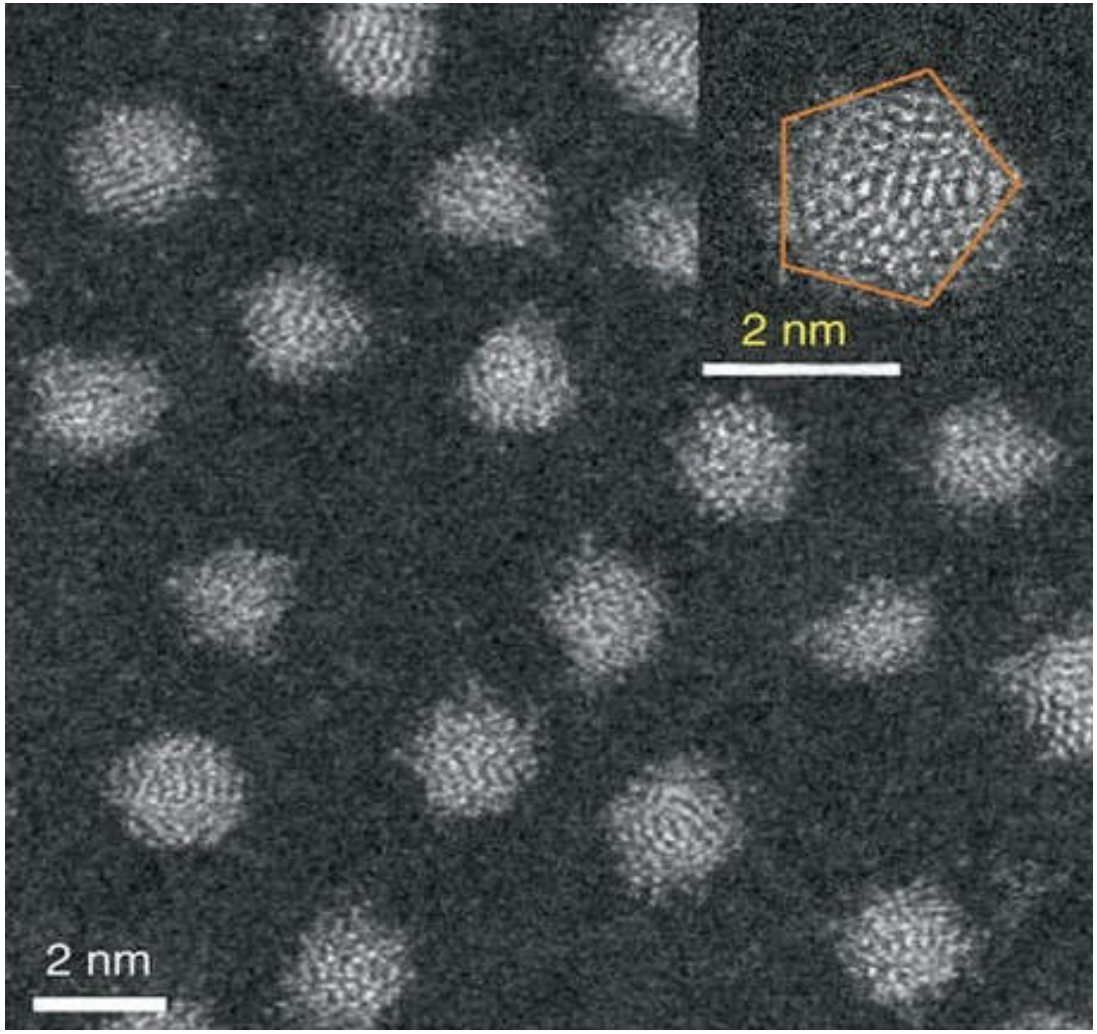


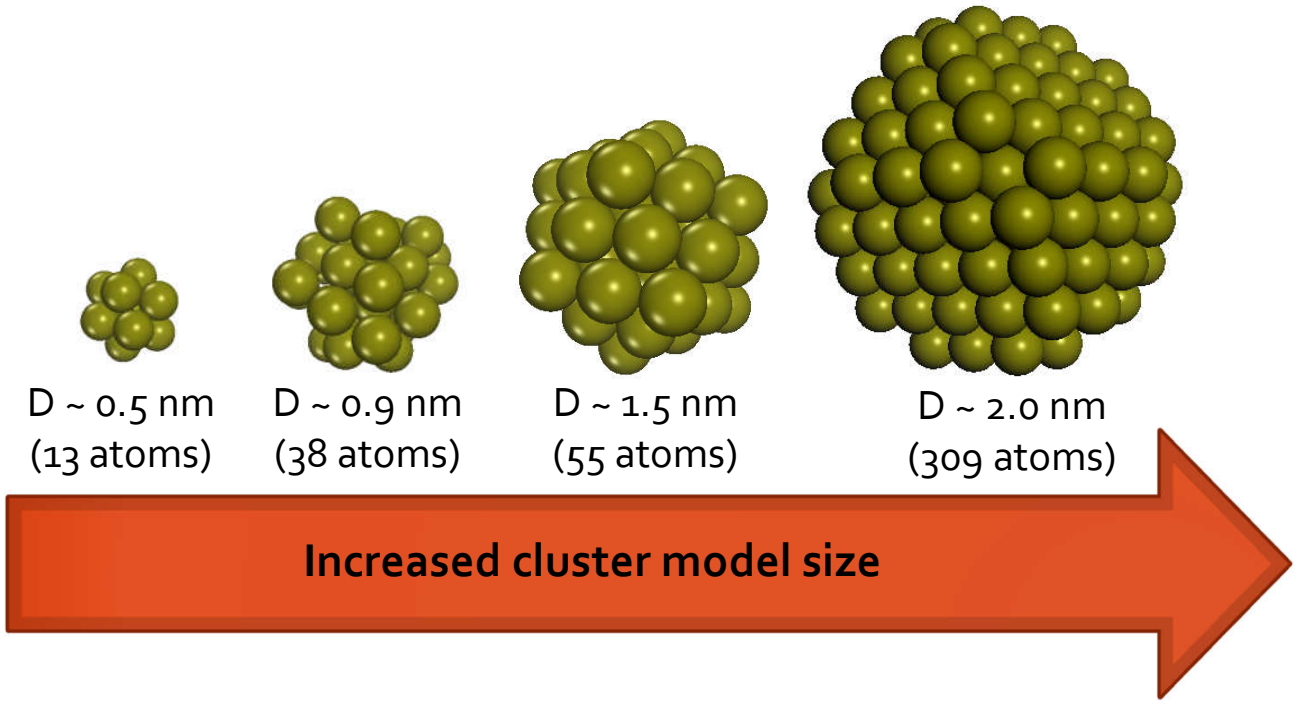
Cluster chemistry:

A finite group of atoms (metal) that are held together mainly, by bonds directly between metal atoms, even though some non-metal atoms may also be intimately associated with the cluster.

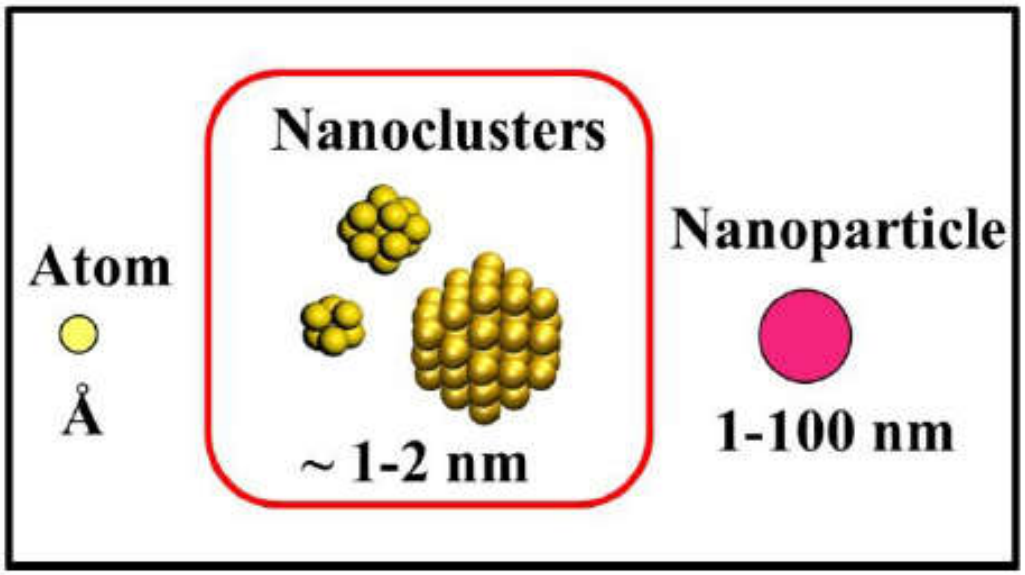
A nanocluster is a nanometer sized particle made up of equal subunits. These subunits can be atoms of a single element, molecules or even combinations of atoms of several elements in subunits with equal stoichiometries (alloys, etc.)

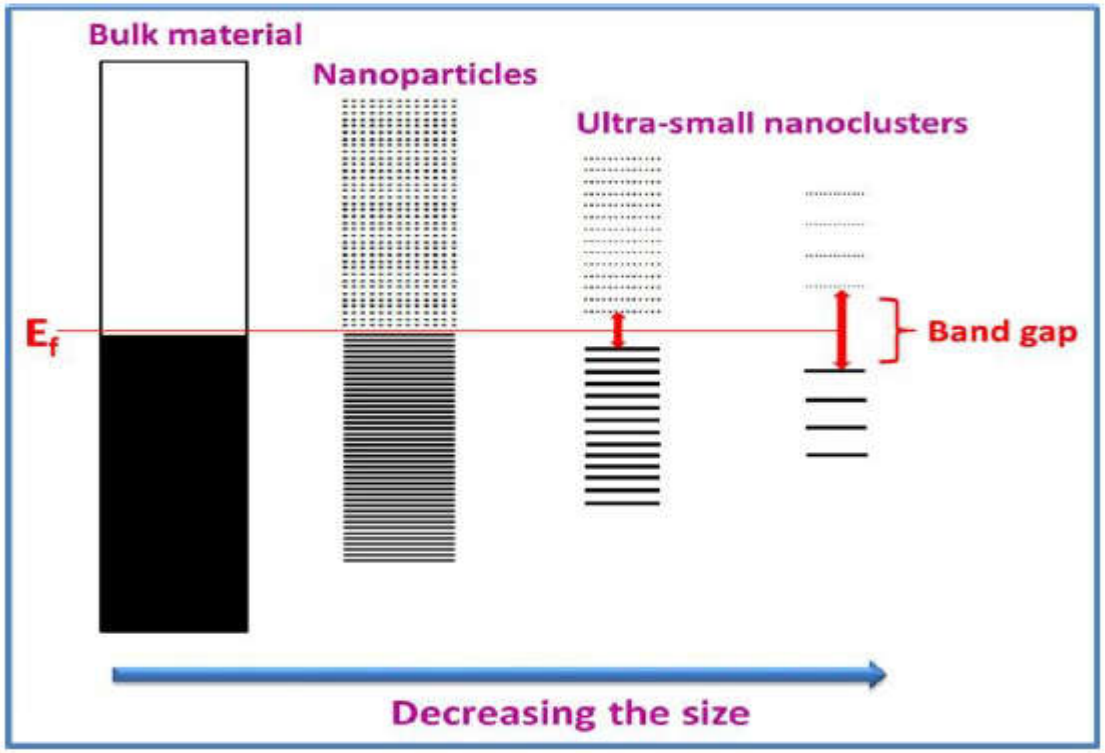
E.g.: Na_n, $(SF_6)_n$, $(H_2O)_n$, $(Cu_3Au)_n$, $(ClCH_3C_6H_3CO_2H)_n$, $(TiO_2)_n$, . . .

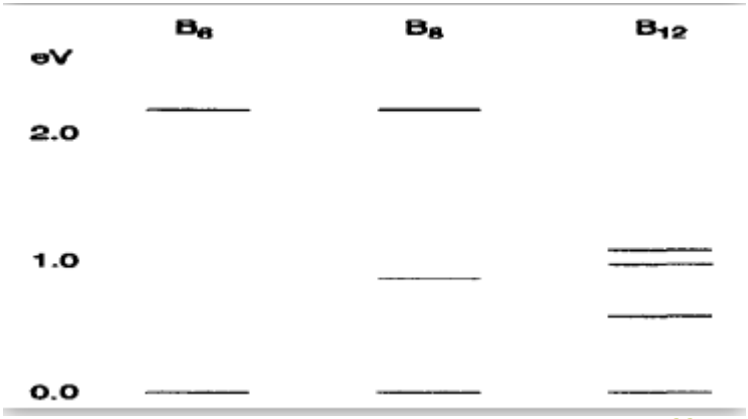

2 nm
2 nm

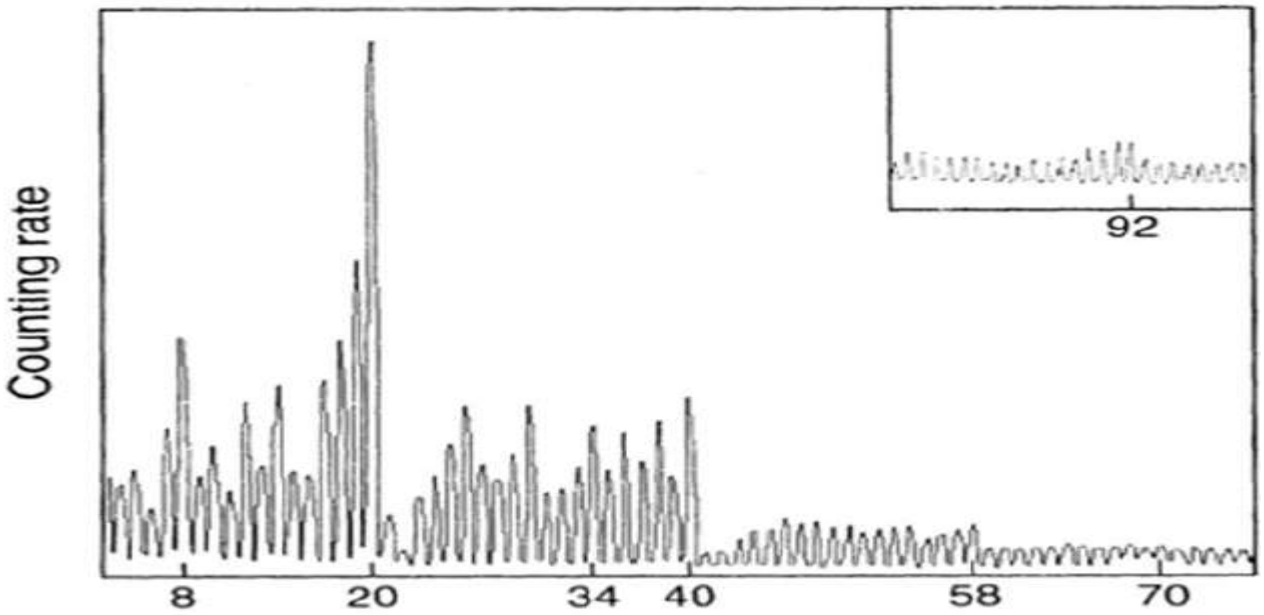

D ~ 0.5 nm
(13 atoms)
D ~ 0.9 nm
(38 atoms)
D ~ 1.5 nm
(55 atoms)
D ~ 2.0 nm
(309 atoms)
Increased cluster model size

Metal nanoclusters are ultra-small (<2 nm) nanoparticles or nano molecules, typically composed of few tens to hundreds of metal atoms protected by ligand molecules such as thiols, phosphines, amines, selenates, etc. Nanoclusters generally denoted as $M_n(L)_m$ (where n and m represent the number of metal atoms and capping ligands respectively).




Bulk material
Nanoparticles
Ultra-small nanoclusters
E_f
Band gap
Decreasing the size

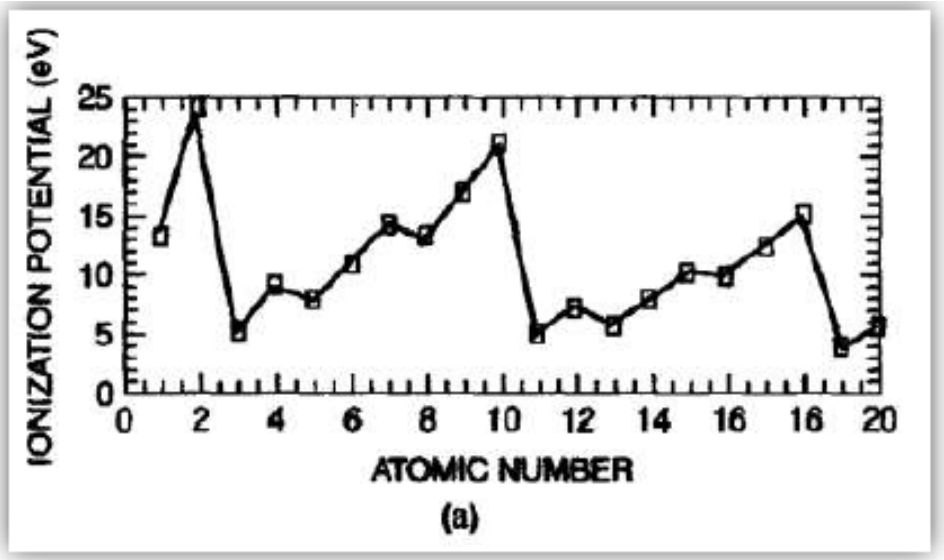

B_6
B_8
B_{12}
eV
2.0
1.0
0.0



Mass Spectra of Sodium Clusters

Sodium clusters with 2, 8, 20, 40, 58, and 92 sodium atoms exhibited relatively larger peaks in the mass spectra than other cluster sizes, and an abrupt decrease in intensity followed.

Mass spectra obtained by Knight and co-workers (1983-85), for alkali metal clusters, showed a number of peaks with high relative intensities ⇒ **Magic Numbers**.

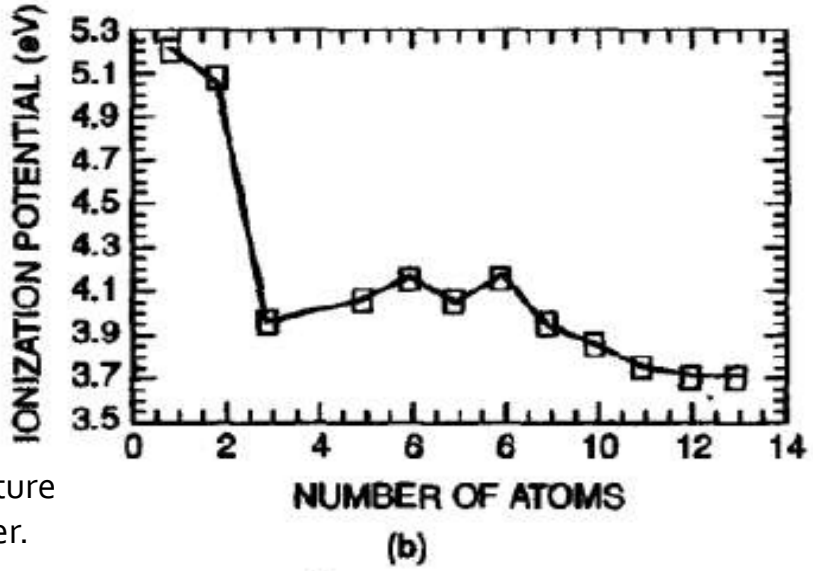


Ionization potential: It is the energy that is necessary to remove the outer electron from the atom.

Maximum ionization potential occurs for the rare gases, because their outer orbital is completely filled.

Peaks are observed at clusters having two and eight atoms.

These numbers are referred as electronic magic number.

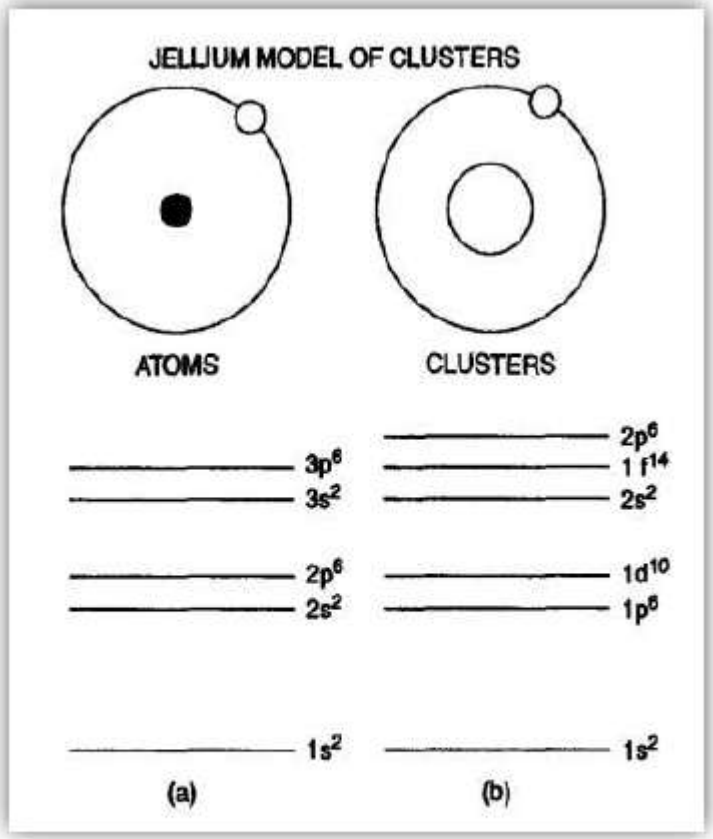


STRUCTURAL MAGIC NUMBER:

For larger clusters the stability is determined by structure and magic number is called as Structural Magic Number.

JELLIUM MODEL:

- ✓ It envisions cluster as a large atom.
- ✓ Positive nuclear charge of each Cluster is assume to be uniformly distributed over a sphere the size of the cluster.
- ✓ Interaction of electron with positive sphere is described as a spherically symmetric potential well.
- ✓ Energy levels can be obtained by solving Schrodinger equation.



A comparison of energy levels of hydrogen atom and Jellium model of clusters

Surface effect

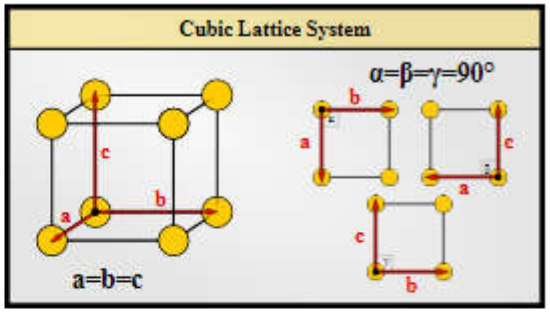
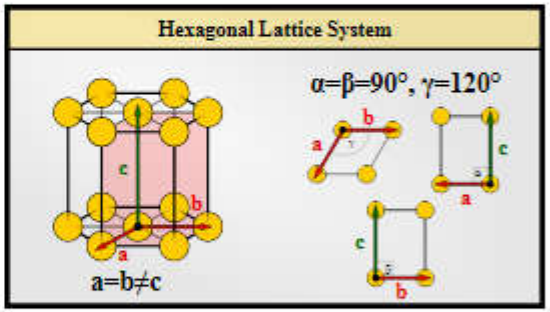
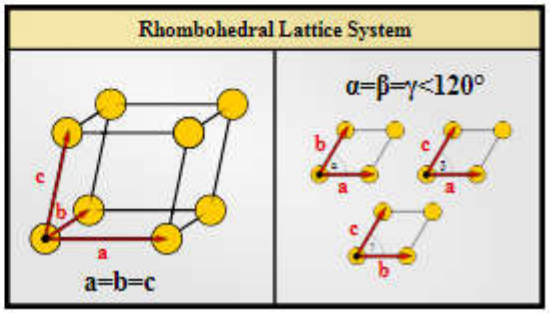
TABLE 2.1 The relation between the total number of atoms in full shell clusters and the percentage of surface atoms

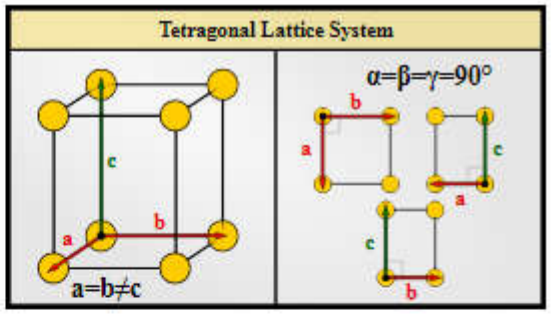
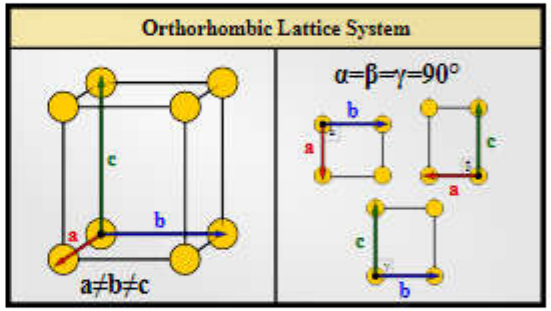
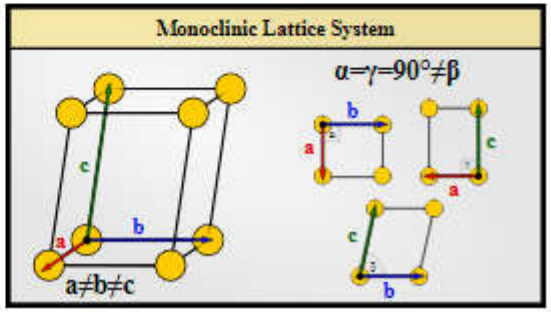
Full-shell Clusters		Total Number of Atoms	Surface Atoms (%)
1 Shell		13	92
2 Shells		55	76
3 Shells		147	63
4 Shells		309	52
5 Shells		561	45
7 Shells		1415	35

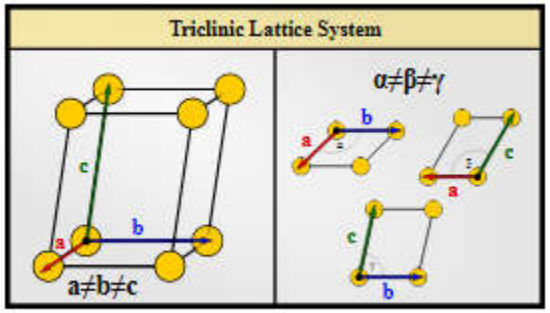
With FCC structure

Crystal systems

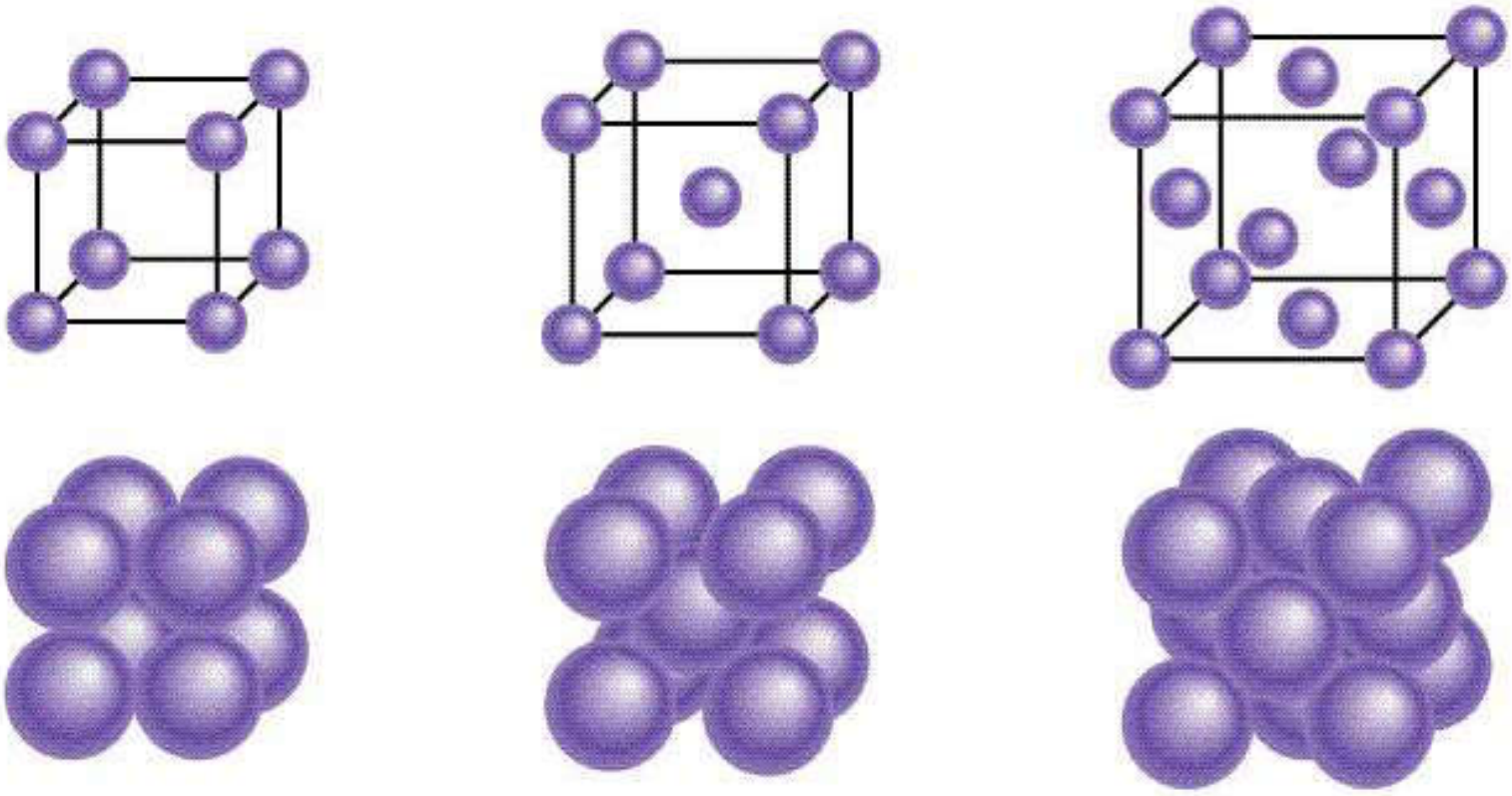
Cubic	Three equal axes, mutually perpendicular $a=b=c \quad \alpha=\beta=\gamma=90^\circ$
Tetragonal	Three perpendicular axes, only two equal $a=b\neq c \quad \alpha=\beta=\gamma=90^\circ$
Hexagonal	Three equal coplanar axes at 120° and a fourth unequal axis perpendicular to their plane $a=b\neq c \quad \alpha=\beta=90^\circ \quad \gamma=120^\circ$
Rhombohedral	Three equal axes, not at right angles $a=b=c \quad \alpha=\beta=\gamma\neq90^\circ$
Orthorhombic	Three unequal axes, all perpendicular $a\neq b\neq c \quad \alpha=\beta=\gamma=90^\circ$
Monoclinic	Three unequal axes, one of which is perpendicular to the other two $a\neq b\neq c \quad \alpha=\gamma=90^\circ\neq\beta$
Triclinic	Three unequal axes, no two of which are perpendicular $a\neq b\neq c \quad \alpha\neq\beta\neq\gamma\neq90^\circ$

Basic Lattice Systems	Edge	Angle	Visualization
Cubic	a=b=c	α=β=γ=90°	
Hexagonal	a=b≠c	α=β=90°, γ=120°	
Rhombohedral	a=b=c	α=β=γ<120°	

Tetragonal	a=b≠c	α=β=γ=90°	
Orthorhombic	a≠b≠c	α=β=γ=90°	
Monoclinic	a≠b≠c	α=γ=90°<β	

Triclinic	a≠b≠c	α≠β≠γ	

Three Types of Cubic Cells



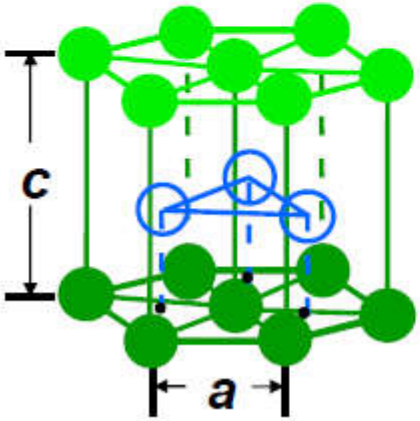
Simple cubic

Body-centered cubic

Face-centered cubic

Hexagonal Close-Packed Structure (HCP)

- ABAB... Stacking Sequence
- 3D Projection

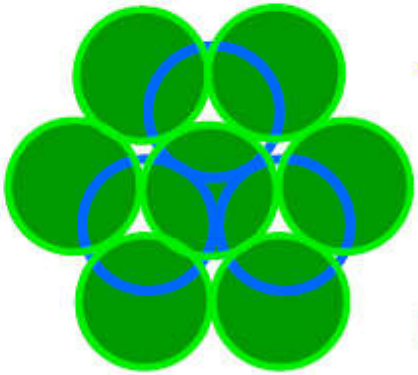


A sites

B sites

A sites

- 2D Projection

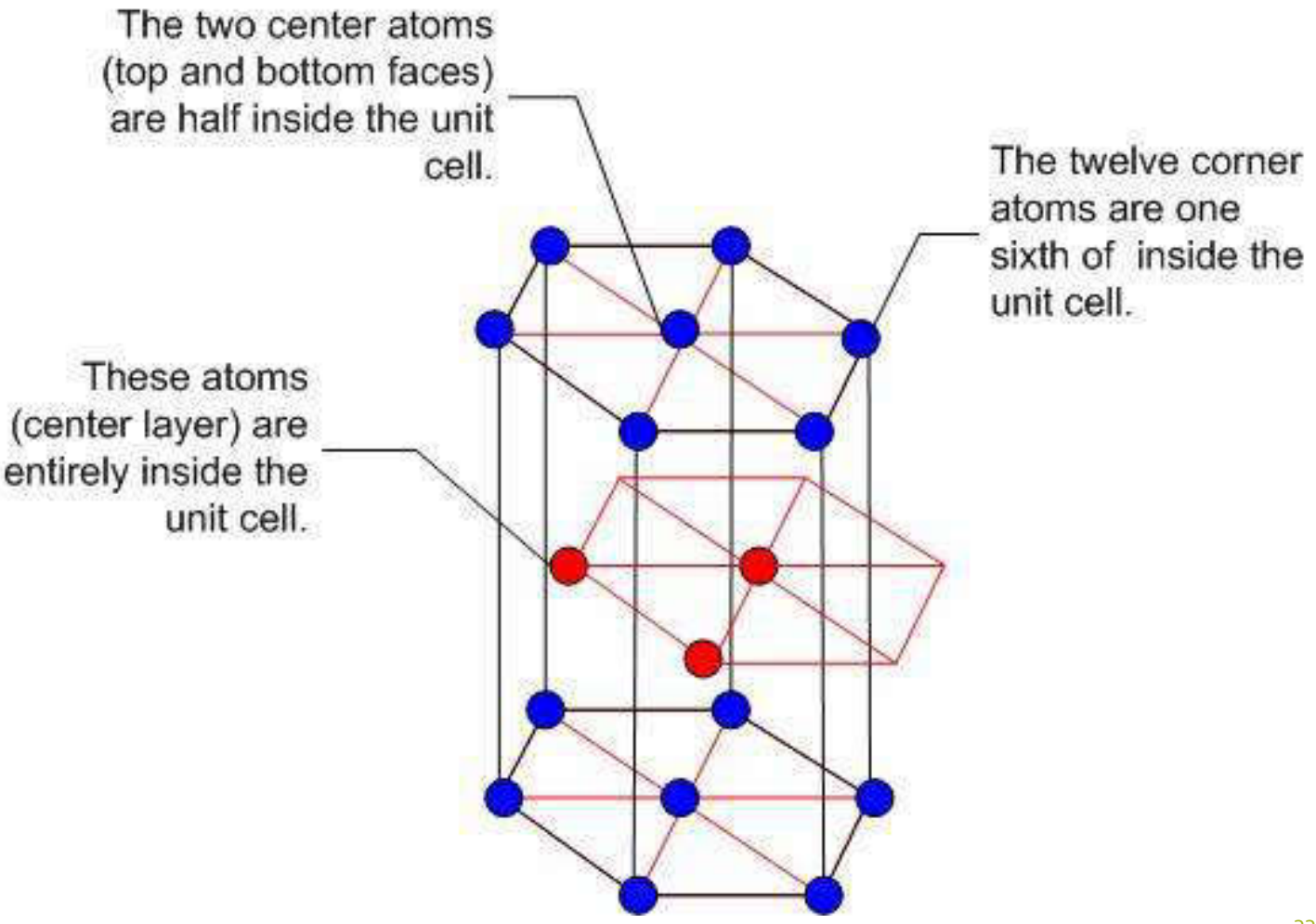


Top layer

Middle layer

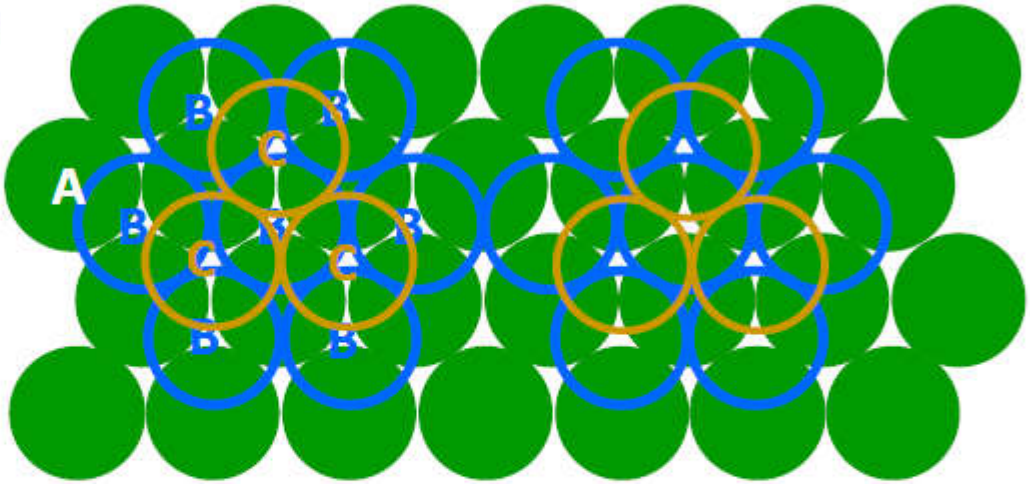
Bottom layer

Hexagonal Close Pack Unit Cell

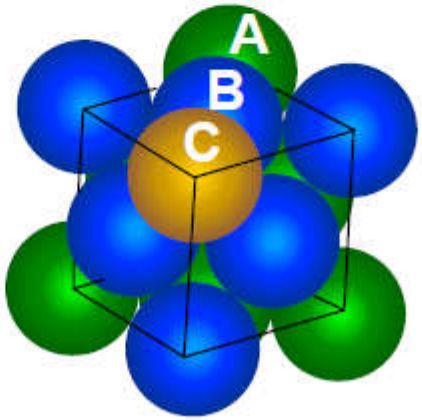


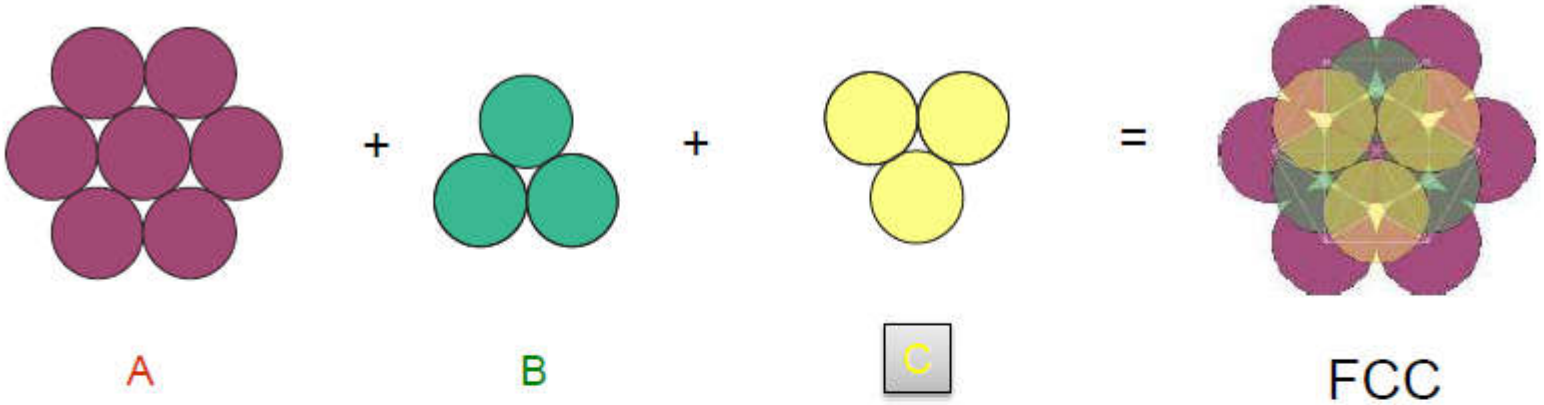
FCC Stacking Sequence

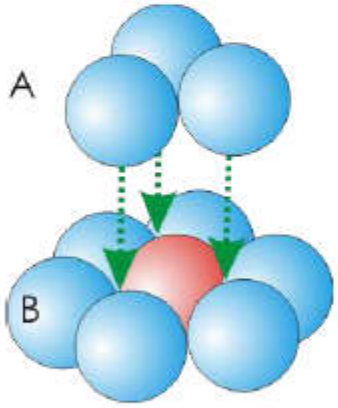
- ABCABC... Stacking Sequence
- 2D Projection

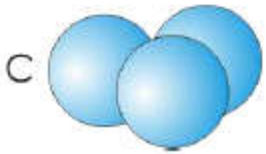


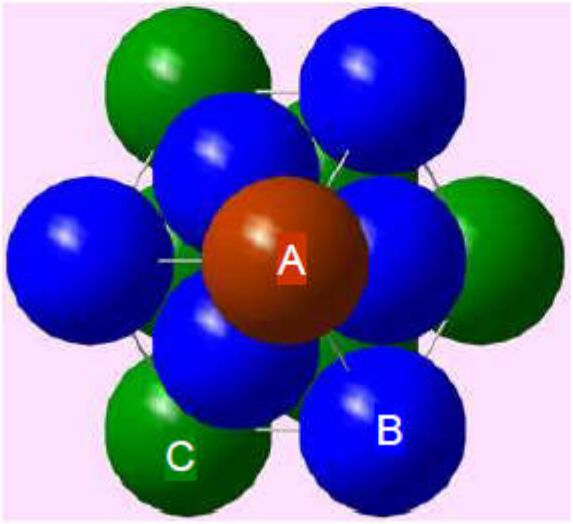
- FCC Unit Cell

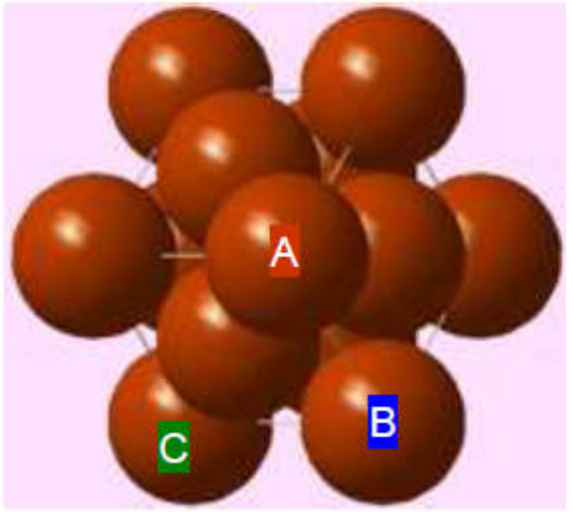


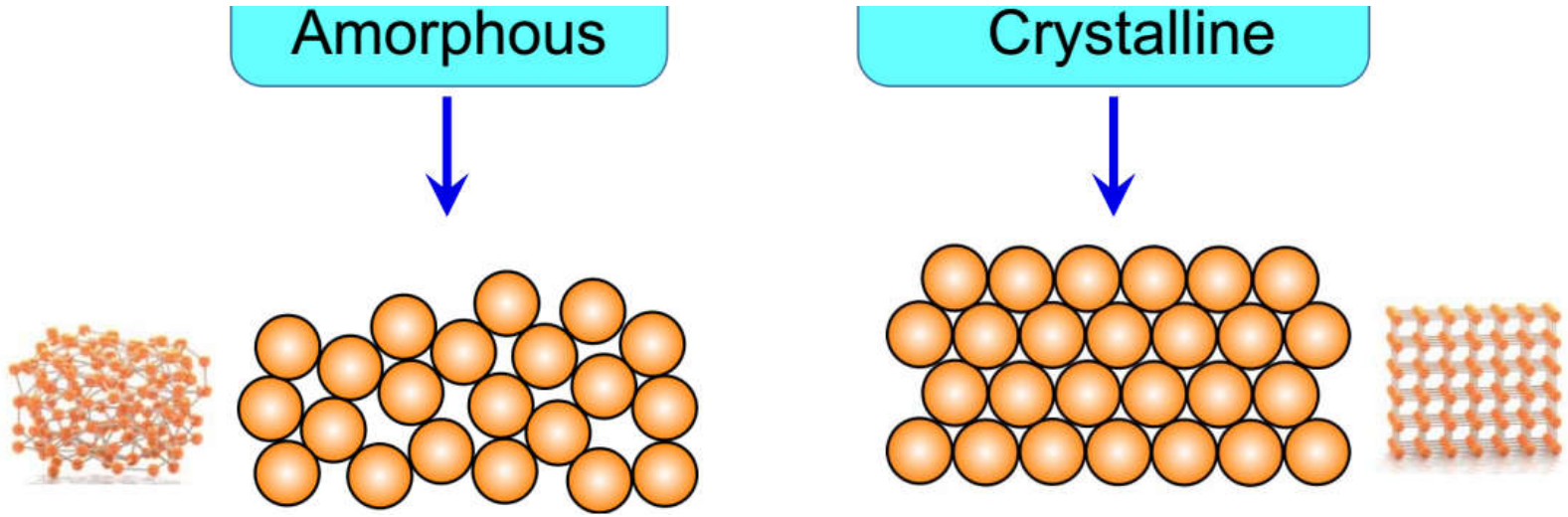

+
+
=
A
B
C
FCC

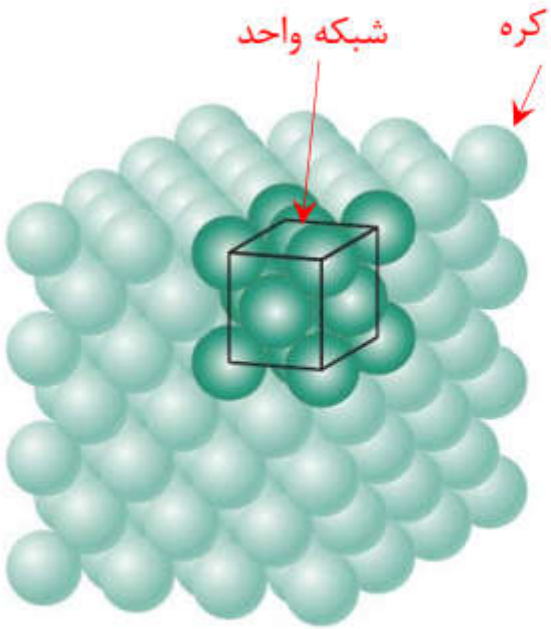

A
B


C

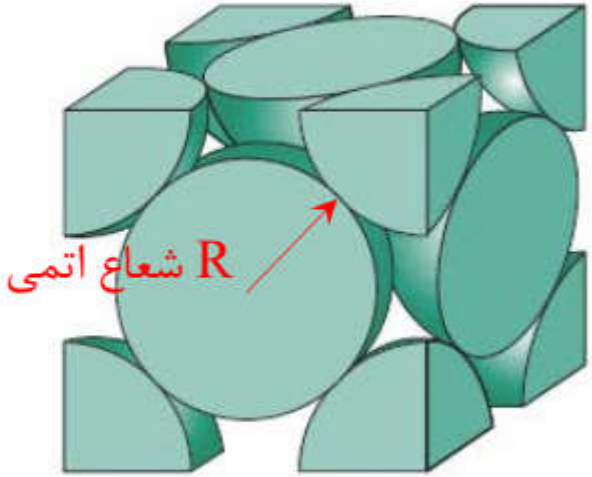

A
C
B


A
C
B


Amorphous
Crystalline

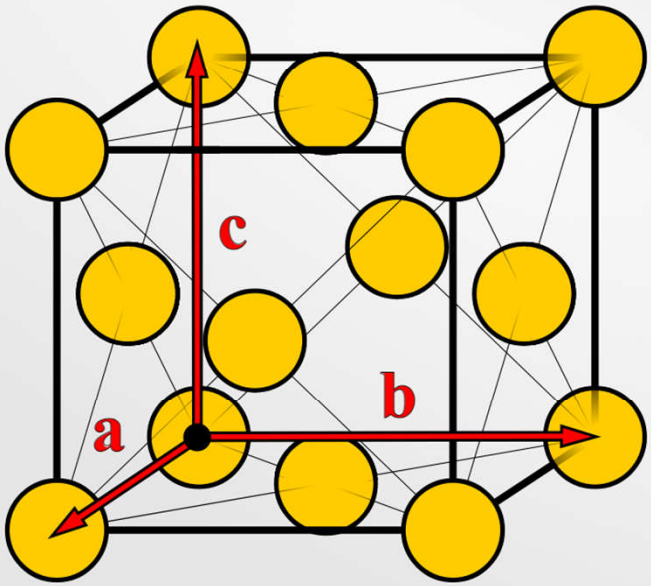


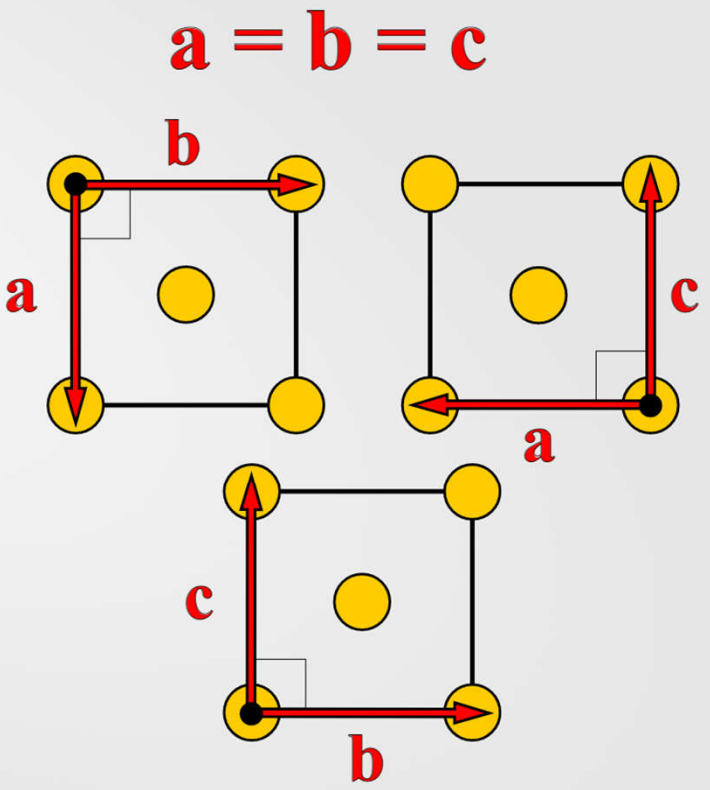
ساختمان سه بعدی
منظم از یک ماده



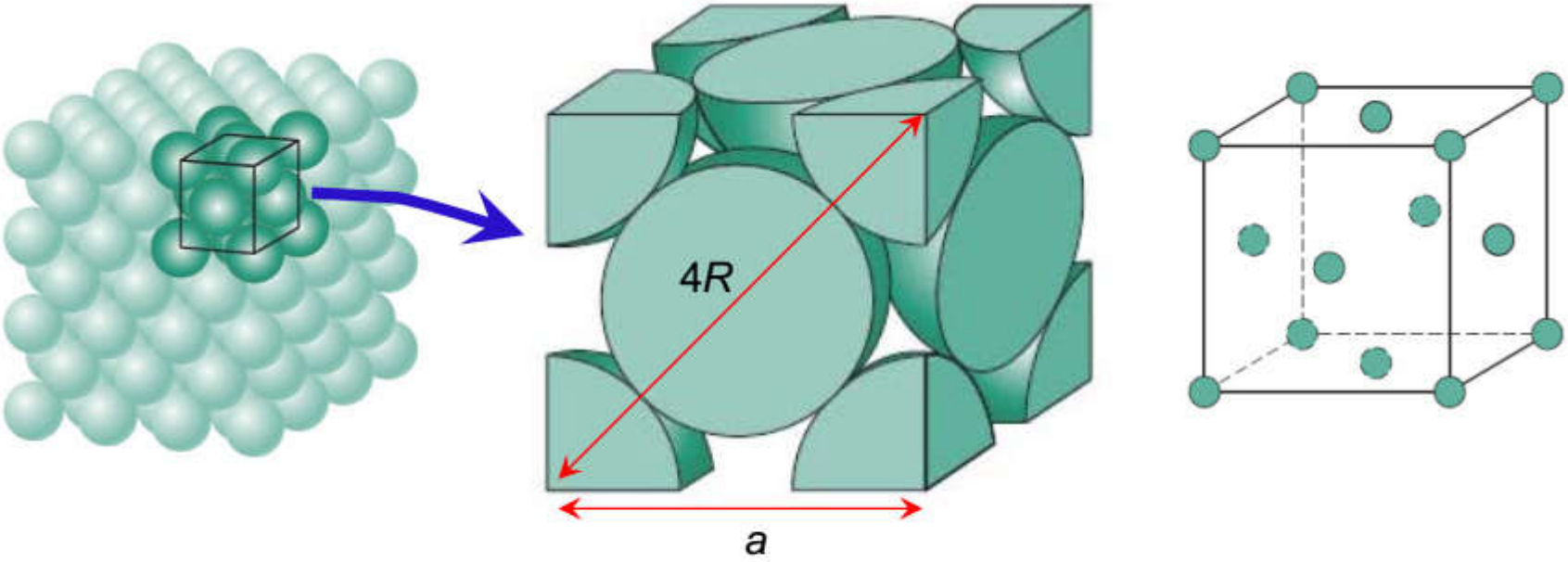
شبکه واحد

Face-Centered Cubic (FCC) Crystal Structure



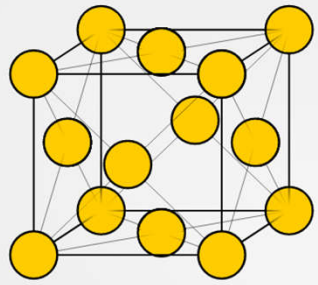


FCC

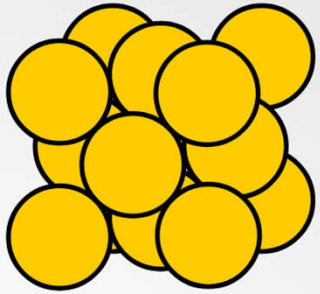


$$4R = \sqrt{2}a \rightarrow a = 2\sqrt{2}R$$

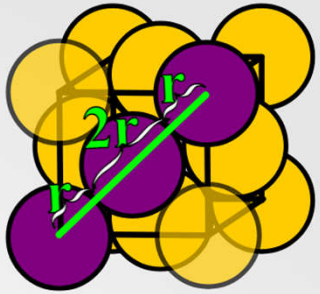
Cu, Au, Ag, Al



FCC Visual Representation with Open Space

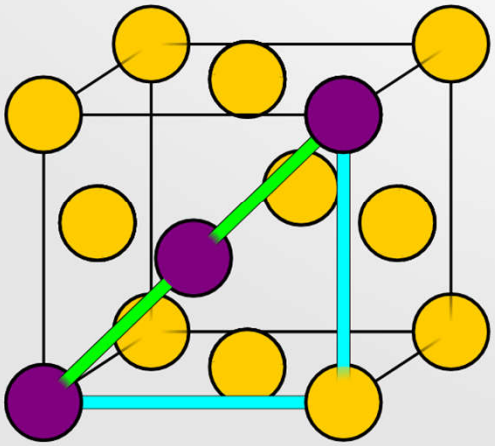


Hard Sphere Model--Atoms Touch



Atoms Touch along the Face Diagonal: Close-Packed Direction

This diagonal has length of 4 radii

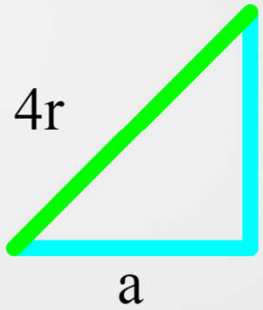


$\frac{1}{2}2r + \frac{1}{2}2r + 2r = 4r$

lattice constant a

Lattice constant is the unit cell side length. All sides are the same length in a cube, so only one lattice constant, a

2D projection along (100)

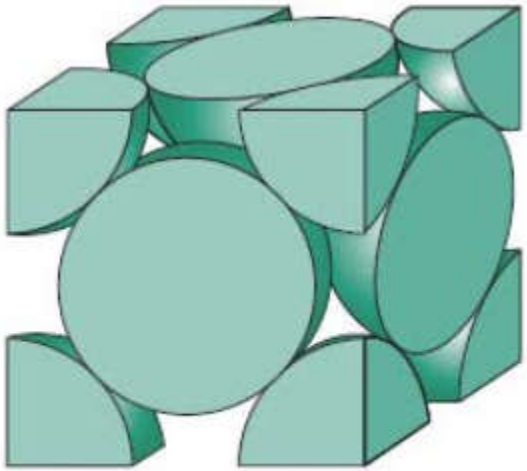


$a^2 + a^2 = (4r)^2$

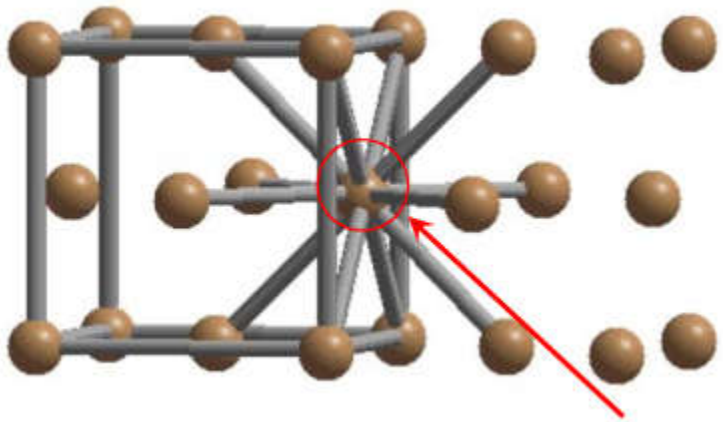
$2a^2 = (4r)^2$

$a = 2\sqrt{2}r$

$$N = N_i + \frac{N_f}{2} + \frac{N_c}{8}$$



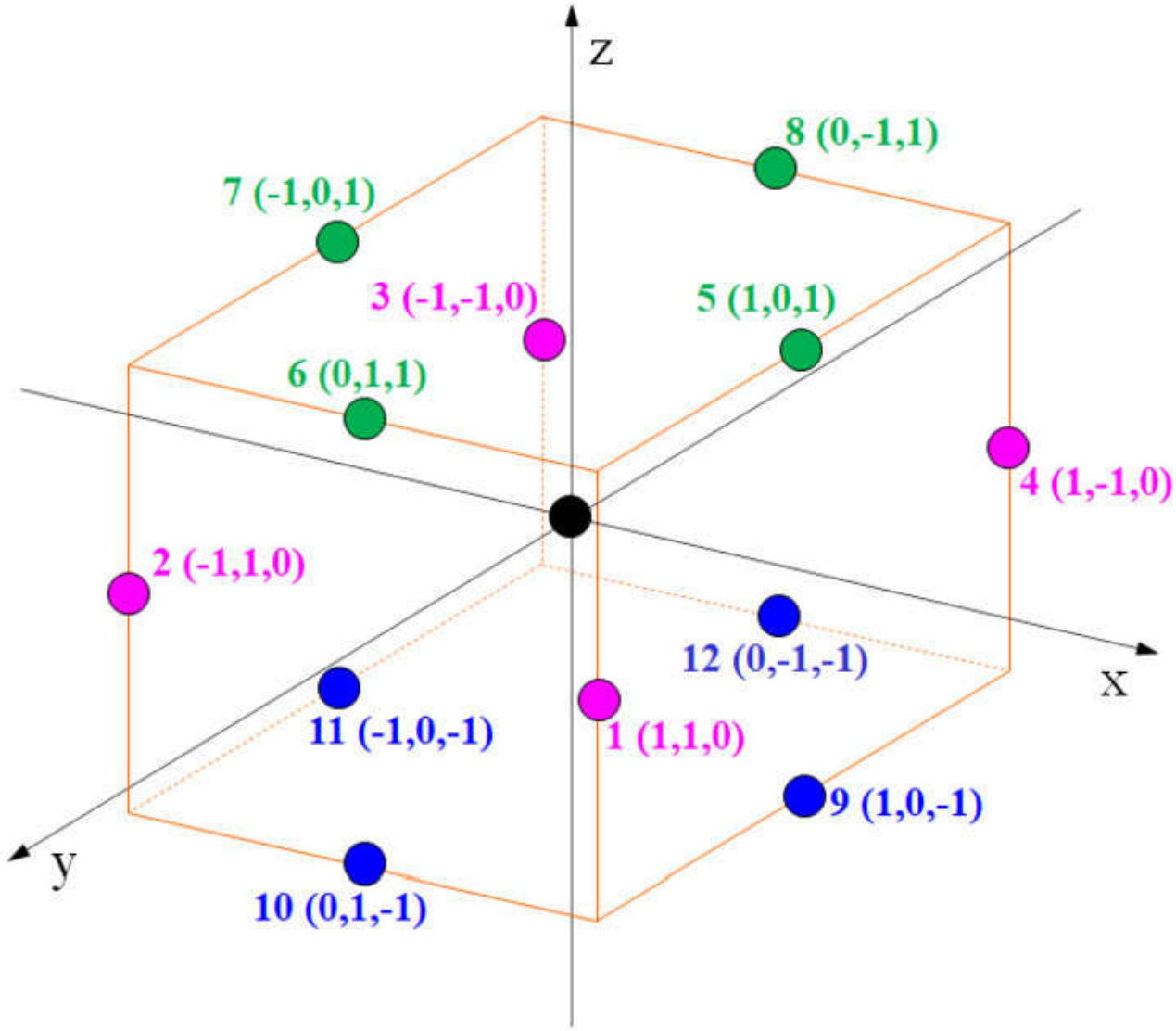
$$N = 0 + \frac{6}{2} + \frac{8}{8} = 4$$



Coordination Number (CN) is the number of nearest neighbors that each atom has.

Coordination Number (CN)= 4+4+4= 12

CN is similar for all atoms


z
8 (0,-1,1)
7 (-1,0,1)
3 (-1,-1,0)
5 (1,0,1)
6 (0,1,1)
4 (1,-1,0)
2 (-1,1,0)
12 (0,-1,-1)
x
11 (-1,0,-1)
1 (1,1,0)
9 (1,0,-1)
y
10 (0,1,-1)

Face-Centered Cubic (FCC)

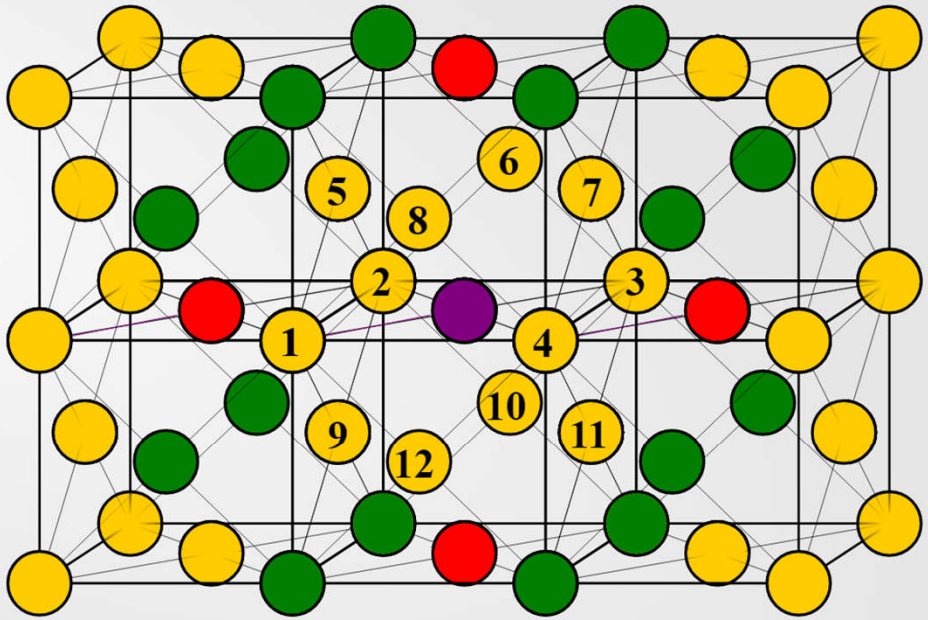
Coordination number: **12**

1, 2, 3, 4, 5, 6, 7
8, 9, 10, 11, 12

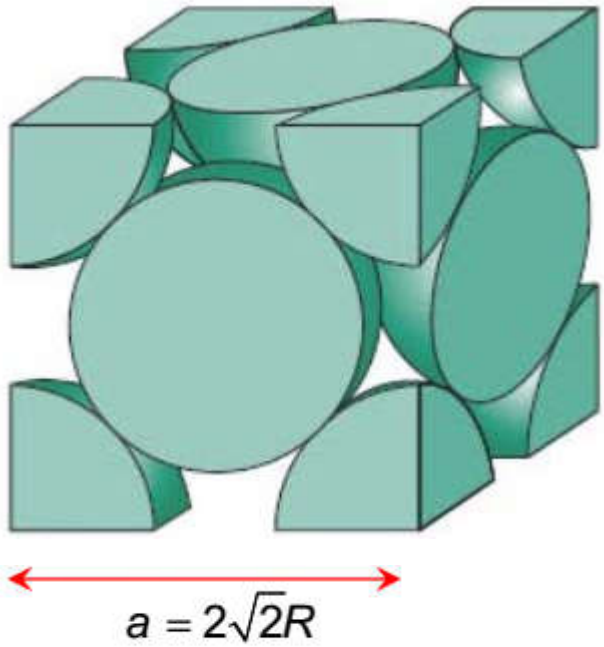
Nearest neighbors (NN)

Next-nearest neighbors (NNN)

Next-next nearest neighbors (NNNN)



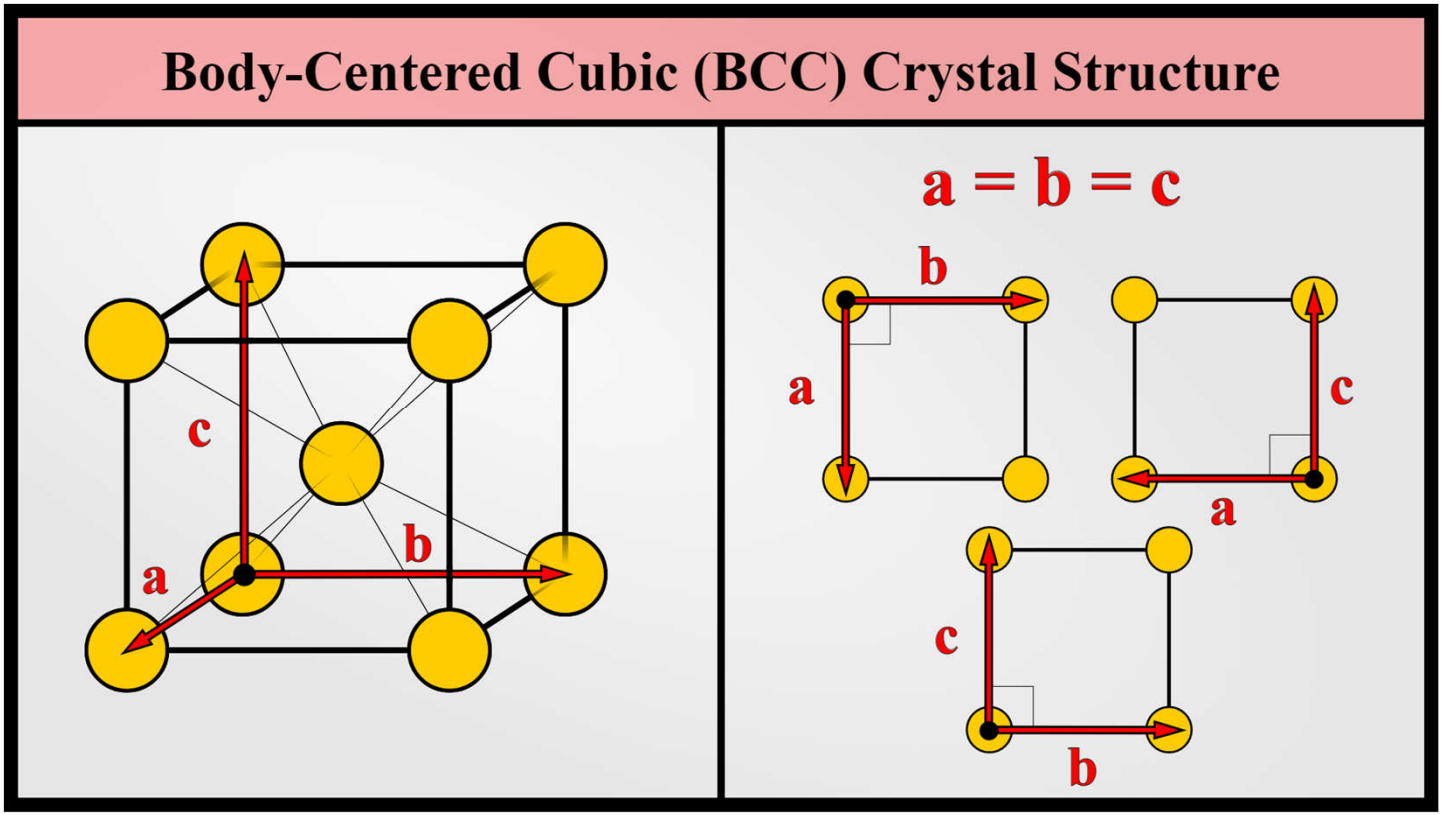
Atomic packing factor (AFP)



AFP = Volume of atoms / Volume of unite cell

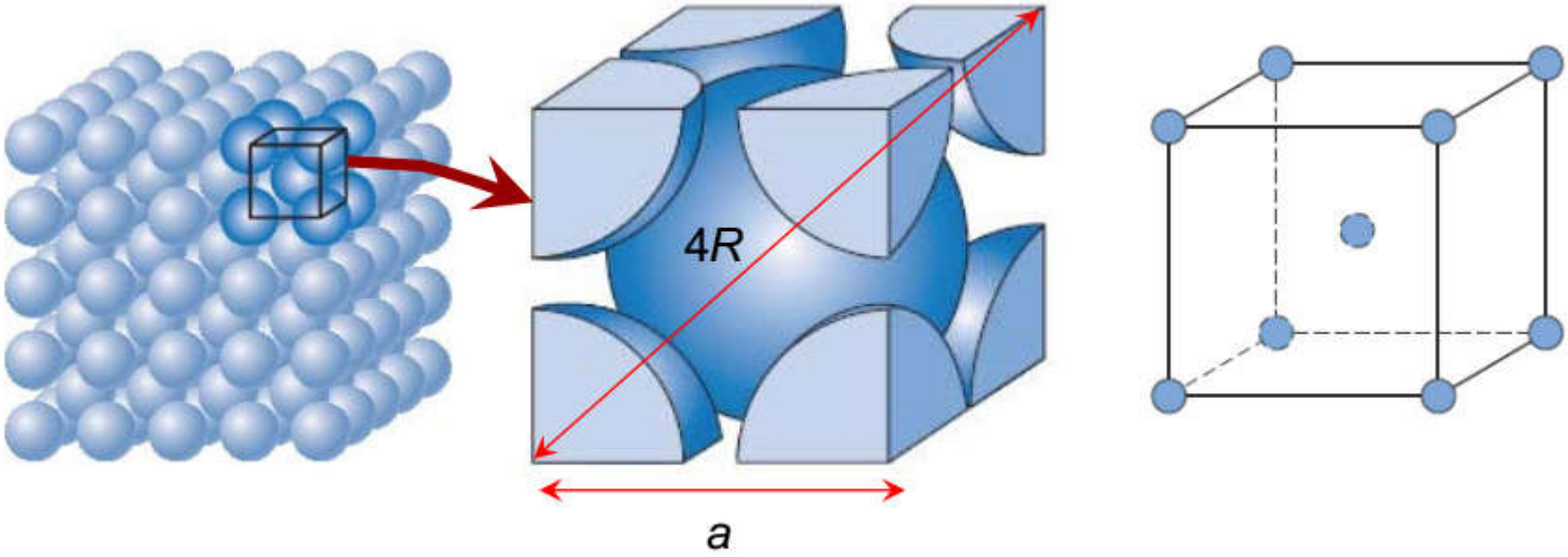
$$AFP = \frac{4 \times \frac{4}{3}\pi R^3}{a^3 = \left(2\sqrt{2}R\right)^3} = 0.74$$

BCC

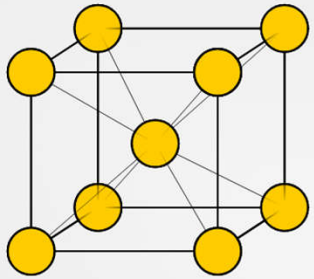


Cr, W, Mo

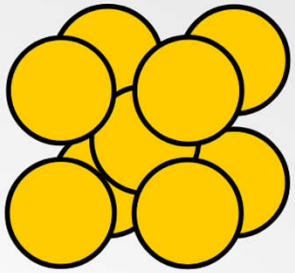
BCC



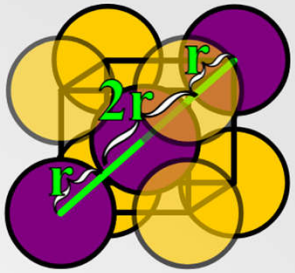
Cr, W, Mo



BCC Visual Representation with Open Space

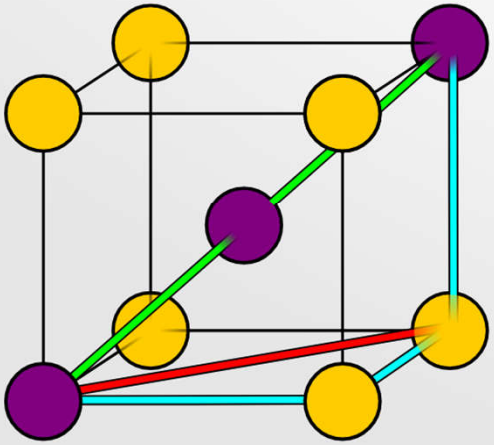


Hard Sphere Model--Atoms Touch



Atoms Touch along the Body Diagonal: Close-Packed Direction

This diagonal has length of 4 radii

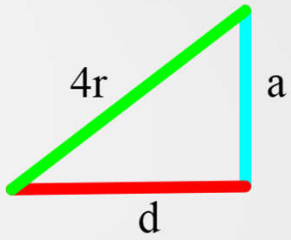


$\frac{1}{2}2r + \frac{1}{2}2r + 2r = 4r$

lattice constant **a**

face diagonal **d**

2D projection along (110)

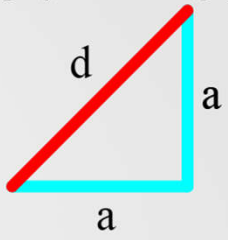


$a^2 + d^2 = (4r)^2$

$3a^2 = (4r)^2$

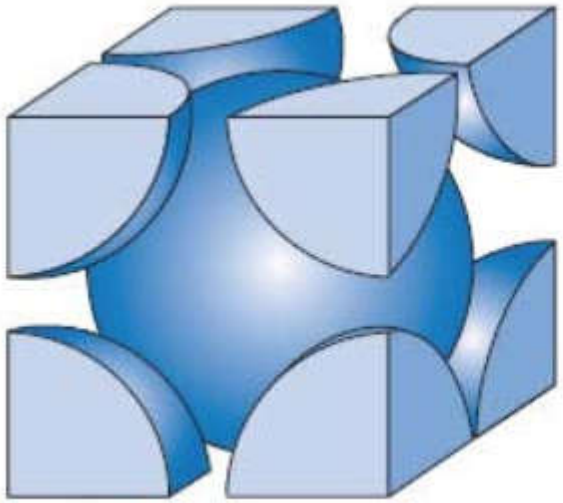
$a = \frac{4}{\sqrt{3}}r$

2D projection along (001)

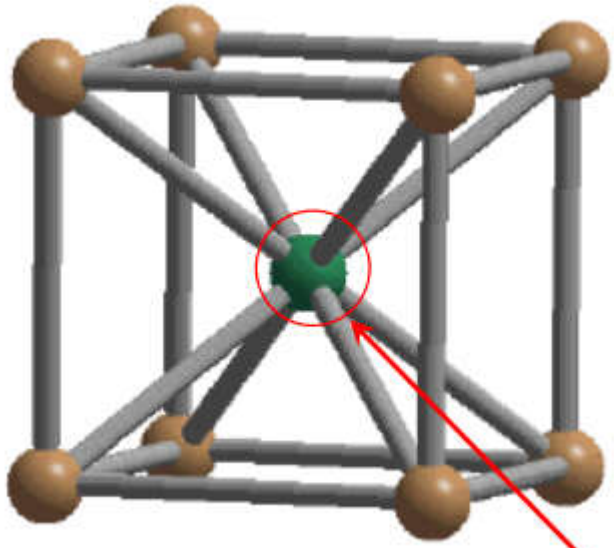


$a^2 + a^2 = d^2$

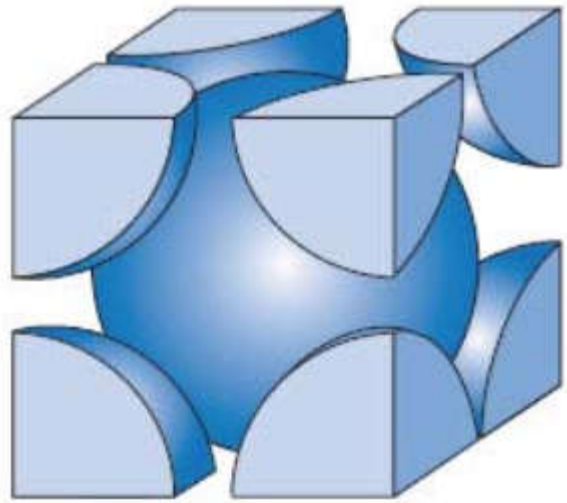
$d^2 = 2a^2$



$$N = 1 + \frac{0}{2} + \frac{8}{8} = 2$$



CN= 4+4=8



$$a = \frac{4R}{\sqrt{3}}$$

$$AFP = \frac{2 \times \frac{4}{3}\pi R^3}{a^3 = \left(\frac{4R}{\sqrt{3}}\right)^3} = 0.68$$

Crystal Structures of Elements at STP

STP - Standard Temperature and Pressure

BCC - Body-centered Cubic
FCC - Face-centered Cubic
HEX - Simple Hexagonal
HCP - Close-packed Hexagonal
DHCP - Double Close-packed Hexagonal
RHO - Rhombohedral

BCT - Body-centered Tetragonal
ORTH - Orthorhombic
DC - Diamond Cubic
DT - Diamond Tetragonal
SC - Simple Cubic
* predicted crystal structure

H HEX																	He HCP
Li BCC	Be HCP											B RHO	C HEX	N complex HCP	O P-cubic	F P-cubic	Ne FCC
Na BCC	Mg HCP											Al FCC	Si DC	P ORTH	S ORTH	Cl complex C-ORTH	Ar FCC
K BCC	Ca FCC	Sc HCP	Ti HCP	V BCC	Cr BCC	Mn α-Mn	Fe BCC	Co HCP	Ni FCC	Cu FCC	Zn HCP	Ga complex F-ORTH	Ge DC	As P-RHO	Se complex HEX	Br complex C-ORTH	Kr FCC
Rb BCC	Sr FCC	Y HCP	Zr HCP	Nb BCC	Mo BCC	Tc HCP	Ru HCP	Rh FCC	Pd FCC	Ag FCC	Cd HCP	In BCT	Sn DT	Sb P-RHO	Te complex HEX	I complex C-ORTH	Xe FCC
Cs BCC	Ba BCC	57-71	Hf HCP	Ta BCC	W BCC	Re HCP	Os HCP	Ir FCC	Pt FCC	Au FCC	Hg RHO	Tl HCP	Pb FCC	Bi RHO	Po SC	At FCC*	Rn FCC*
Fr BCC*	Ra BCC	89-103	Rf HCP*	Db BCC*	Sg BCC*	Bh HCP*	Hs HCP*	Mt FCC*	Ds BCC*	Rg BCC*	Cn HCP*	Nh HCP*	Fl FCC*	Mc UNKNOWN	Lv UNKNOWN	Ts UNKNOWN	Og FCC*

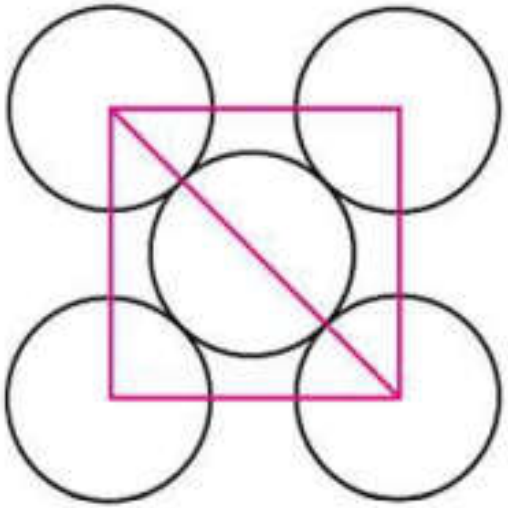
La DHCP	Ce DHCP	Pr DHCP	Nd DHCP	Pm DHCP	Sm complex RHO	Eu BCC	Gd HCP	Tb HCP	Dy HCP	Ho HCP	Er HCP	Tm HCP	Yb FCC	Lu HCP
Ac FCC	Th FCC	Pa BCT	U ORTH	Np ORTH	Pu MONO	Am DHCP	Cm DHCP	Bk DHCP	Cf DHCP	Es FCC	Fm FCC*	Md FCC*	No FCC*	Lr HCP*

Solid state at STP

Liquid state at STP

Gaseous state at STP

The fcc unit cell is a cube with atoms at each of the corners and in the center of each face, as shown here. Copper has the fcc crystal structure. Assume an atomic radius of 128 pm for a Cu atom.



(a) What is the length of the unit cell of Cu?
(b) What is the volume of the unit cell?
(c) How many atoms belong to the unit cell?
(d) What percentage of the volume of the unit cell is occupied?
(e) What is the mass of a unit cell of copper?
(f) Calculate the density of copper.

(a) Unit cell length: we note from the picture that the hypotenuse of the right triangle equals 4×r.

$$L^2 + L^2 = (4r)^2 = 16 \cdot (128\ \text{pm})^2 = 2.621 \times 10^5$$

$$L = \sqrt{2.621 \times 10^5 / 2} = 362\ \text{pm}$$

(b) volume = $(362\ \text{pm})^3 = 4.74 \times 10^7\ \text{pm}^3$

(c) 8 corners × 1/8 + 6 faces × ½ = 4 atoms/unit cell.

(d) Volume % is the ratio between the volume taken up by the atoms and the volume of the unit cell.

$$\frac{\text{vol of atoms}}{\text{vol of cells}} = \frac{4 \times (4/3)\pi\,(128\ \text{pm})^3}{4.74 \times 10^7\ \text{pm}^3} \times 100 = 74\%$$

(e)

$$\frac{\text{mass of Cu}}{\text{unit cell}} = \frac{4\ \text{atoms}}{\text{unit cell}} \times \frac{1\ \text{mol Cu}}{6.022 \times 10^{23}\ \text{atoms}} \times \frac{63.546\ \text{g Cu}}{1\ \text{mol Cu}} = 4.221 \times 10^{-22}\ \text{g}$$

(f) D = m/V

$$D = \frac{4.221 \times 10^{-22}\ \text{g Cu}}{4.74 \times 10^7\ \text{pm}^3} \times \frac{(1 \times 10^{-10}\ \text{pm})^3}{(1\ \text{cm})^3} = 8.91\ \text{g/cm}^3$$